

JP 46041033

L1 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN  
ACCESSION NUMBER: 1972:406123 CAPLUS Full-text  
DOCUMENT NUMBER: 77:6123  
TITLE: Catalysts for preparation of poly(ethylene terephthalate)  
INVENTOR(S): Kobayashi, Hidehiko; Kawamoto, Hiroshi  
PATENT ASSIGNEE(S): Asahi Chemical Industry Co., Ltd.  
SOURCE: Jpn. Tokkyo Koho, 9 pp.  
CODEN: JAXXAD  
DOCUMENT TYPE: Patent  
LANGUAGE: Japanese  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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JP 46041033	B4	19711203	JP	19680315 <--
AB	A mixture of Mn borate esters and alkaline earth salts of metaantimonites was an effective catalyst system for both transesterification and condensation. Thus, 436.5 parts di-Me terephthalate, 251.1 parts ethylene glycol, 0.032% (based on transesterified product) of a manganese borate ester $\text{Mn}[\text{B}(\text{OCH}_2\text{CH}_2\text{OH})(\text{OR})_3]_2$ (R = cyclohexyl) [34975-88-7], and 0.01% magnesium antimonite $[\text{Mg}(\text{SbO}_2)_2]$ [34975-89-8] were heated at 100-245.deg., heated in 1 hr to 280.deg./13-30 mm under N, and heated at 280.deg./0.1 mm to give poly(ethylene terephthalate) [25038-59-9] with intrinsic viscosity 0.75 dl/g and improved whiteness.			

**Patent Number(s):** JP47039497-A; JP78001320-B

**Title:** Polyester mfr - using antimony mercapto or thio carboxylates as catalyst

**Patent Assignee Name(s) and Code(s):** MITSUBISHI RAYON CO LTD (MITR-C); MITR (MITR-C)

**Derwent Primary Accession Number:** 1973-49407U [21]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

An Sb salt of alpha-mercaptocarboxylate or thio-alpha, beta-dicarboxylate is used as a polycondensation catalyst of bis (beta-hydroxyethyl) terephthalate to give polyester with improved whiteness and transparency suitable for spinning. E.g. a soln. of Ph2C(SH)CO2H in EtOH was added slowly to a soln. of (EtO)3Sb in EtOH, and the mixt. heated at 60 degrees to give ethoxyantimony diphenylthioglycolate (I). (I) in ethylene glycol (II) was added to an ester-exchanged mixt from di-Me terephthalate and (II) and the mixt. was polycondensed to give a transparent slightly yellow poly(ethylene terephthalate) which had an increased intrinsic viscosity at 25 degrees C than that mfd. using Sb2O3 as catalyst.

**International Patent Classification:** C08G-063/36

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds); E12 (Organometallics); F01 (Threads and fibres, natural or artificial; spinning)

**Derwent Manual Code(s):** A02-A07; A05-E04A; E05-J; F01-D04

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP47039497-A			197335		
JP78001320-B	18 Jan 1978		197806		

**Priority Application Information and Date:**

JP028665	30 Apr 1971
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**Patent Number(s):** JP47042989-A; JP75015511-B

**Title:** Polyesters with improved colour tone - synthesized using antimony catalysts

**Patent Assignee Name(s) and Code(s):** MITSUBISHI RAYON CO LTD (MITR-C); (MITR-C)

**Derwent Primary Accession Number:** 1973-56945U [39]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

An Sb salt of oxalic acid, beta-hydroxycarboxylic acid, alpha, alpha-dicarboxylic acid, or thio acid analogue was used as a polyester condens. catalyst to give fibre grade polyester with good whiteness and transparency in good yield. In an example 8.67 pts. ethoxyantimony oxalate (I) in 200 pts. ethylene glycol (II) was added to a ester-exchanged mixt. from di-Me terephthalate 10,000 (II) 7500 and Mg(OAc)<sub>2</sub> 6 pts. cntg. 3.2 pts. (MeO)<sub>3</sub>PO, and the mixt. polycondensed to give poly(ethylene terephthate) (III) with intrinsic viscosity (25 degrees 1:1 phenol C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>) 0.743 and good whiteness cf 0.672 and greyish discolouration for similarly prepd. (III) with 5 pts. Sb<sub>2</sub>O<sub>3</sub> in place of (I).

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds); F01 (Threads and fibres, natural or artificial; spinning)

**Derwent Manual Code(s):** A02-A07; A05-E01A; F01-D04

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP47042989-A			197339		
JP75015511-B	05 Jun 1975		197527		

**Priority Application Information and Date:**

JP030939	10 May 1971
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**Patent Number(s):** NL7107667-A; CA965091-A; AR202689-A; CH573925-A;  
JP77018716-B; **JP48005798-A**

**Title:** Tetracyclic piperazine derivs - biologically active

**Patent Assignee Name(s) and Code(s):** AKZO NV (ALKU-C)

**Derwent Primary Accession Number:** 1972-81815T [21]

**Patents Cited by Inventor:** 0

**Citing Patents:** 2

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Biologically active compds. of formula (I): are prepd. by condensing compds of formula (II): with 1,2 dihaloethanes in an aprotic solvent of ET >40 (e.g. a dihaloethane) at 70-140 degrees, where R1 and R2 = H, OH, acyloxy, lower alkyl, lower alkoxy, or CF3; R3 = H, lower alkyl, lower aralkyl or -(CH2)nNR4R5 where n = 1-4, and R4 and R5 = lower alkyl, or NR4R5 = a heterocyclic residue; and Q = a single bond, CH2, CH2CH2, -CH2=CH-, O, S or NR, where R = lower alkyl.

**International Patent Classification:** C07D-057/24; C07D-099/02; C07D-241/36;  
C07D-487/04; C07D-498/04; C07D-513/04

**Derwent Class:** B02 (Fused ring heterocyclics)

**Derwent Manual Code(s):** B06-D18; B06-E05; B06-F05

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
NL7107667-A			197252		
CA965091-A	25 Mar 1975		197515		
AR202689-A	15 Jul 1975		197613		
CH573925-A	31 Mar 1976		197619		
JP77018716-B	24 May 1977		197724		
JP48005798-A	24 Jan 1973		198347		

**Priority Application Information and Date:**

NL007667	04 Jun 1971
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# JP 48007272

L2 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN  
 ACCESSION NUMBER: 1973:547022 CAPLUS Full-text  
 DOCUMENT NUMBER: 79:147022  
 TITLE: High polymerization degree polyesters  
 INVENTOR(S): Shima, Takeo; Urasaki, Takanori; Kurusu, Fukashi  
 PATENT ASSIGNEE(S): Teijin Ltd.  
 SOURCE: Jpn. Tokkyo Koho, 4 pp.  
 CODEN: JAXXAD  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 48007272	B4	19730303	JP 1968-72258	19681004 ←

AB The d.p. of poly(ethylene terephthalate) (I) [25038-59-9] is increased by polymerization in the presence of 0.001-0.3 mole % (based on acid) Sb compound and a specified amount of diaryl carbonate. Thus, the transesterification product from 250 parts di-Me terephthalate and 166 parts ethylene glycol is heated with 0.06 part antimony trioxide [1309-64-4] and 0.06 part H3PO3 2.5 hr

at 280.deg./<1 mm, combined with 1 part diphenyl carbonate [102-09-0], heated 30 min at <1 mm, combined with 12.5 parts glycol and 0.06 part Sb2O3, and heated 70 min in vacuo to give I; inherent viscosity 1.12.

**Patent Number(s):** BE766653-A; NL7106001-A; DE2121808-A; FR2088367-A;  
**JP48026955-A; GB1351176-A**

**Title:** High protein food from skimmed milk

**Patent Assignee Name(s) and Code(s):** DUMONT WA, JULIEN J-P (DUM-I)

**Derwent Primary Accession Number:** 1971-72090S [22]

**Patents Cited by Inventor:** 0

**Citing Patents:** 5

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

High protein food prepd. by heating skimmed milk at 70-150 degrees C pref. 90 degrees C with a non-toxic calcium salt pref. 0.2 wt.% CaCl<sub>2</sub> followed by separating the ppt. from the whey to give a product of 55-80 wt.% water content which may be subsequently increased.

Preferred product has C.V. 1247 cal/g. and a compsn. 20.0% proteins, 6.4% lactose, 2.6% mineral salts and 71% water.

**International Patent Classification:** A23C-009/00; A23J-000/00

**Derwent Class:** D13 (Other foodstuffs and treatment); E33 (Compounds of Be, Mg, Ca, Sr, Ba, Ra, Sc, Y, La, Ac, Al, lanthanides (Rare-earths), Th)

**Derwent Manual Code(s):** D03-B; D03-F; E34-D

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
BE766653-A			197145		
NL7106001-A			197147		
DE2121808-A			197148		
FR2088367-A			197212		
<b>JP48026955-A</b>			197329		
GB1351176-A	24 Apr 1974		197417		

**Priority Application Information and Date:**

CA082065	06 May 1970
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L3 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN  
 ACCESSION NUMBER: 1974:426257 CAPLUS Full-text  
 DOCUMENT NUMBER: 81:26257  
 TITLE: Polyester  
 INVENTOR(S): Kobayashi, Fumio; Matsukura, Kazuo; Tomita, Kosuke;  
 Yamaguchi, Ryoza  
 PATENT ASSIGNEE(S): Unitika Ltd.  
 SOURCE: Jpn. Tokkyo Koho, 3 pp.  
 CODEN: JAXXAD  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 48031991	B	19731003	JP 1967-68190	19671023 <--
			JP 1967-68190	19671023

PRIORITY APPLN. INFO.:

AB Polyesters with increased transparency are prepared by polycondensing dimethyl terephthalate (I) with ethylene glycol (II), in combination with or without Me p-( $\beta$ -hydroxyethoxy)benzoate, in the presence of known polycondensation catalysts (antimony trioxide [1309-64-4] or germanium dioxide [1310-53-8]), alkaline earth metal compds., and selenium dioxide [7446-08-4] or selenic acid [7783-08-6]. Thus, a mixture of I 1, II 2, and Ca(OAc)<sub>2</sub> 8 .tim. 10<sup>-4</sup> mole was heated 5 hr at 180-210.deg. under N, mixed with 8 .tim. 10<sup>-4</sup> mole SeO<sub>2</sub> and 2 .tim. 10<sup>-4</sup> mole Sb<sub>2</sub>O<sub>3</sub>, and heated 4 hr at 280.deg./0.1mm, giving colorless poly(ethylene terephthalate) [25038-59-9] with intrinsic viscosity (1:1 PhOH-C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, 20.deg.) 0.87.

L4 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN  
 ACCESSION NUMBER: 1974:506333 CAPLUS Full-text  
 DOCUMENT NUMBER: 81:106333  
 TITLE: Polyester  
 INVENTOR(S): Chimura, Kazuchika; Ito, Kazuo; Takashima, Shunichi;  
 Shindo, Tamao; Kawashima, Masao  
 PATENT ASSIGNEE(S): Mitsubishi Rayon Co., Ltd.  
 SOURCE: Jpn. Tokkyo Koho, 4 pp.  
 CODEN: JAXXAD  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 2  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 48038634	B	19731119	JP 1969-59873	19690729 <--
BE 748781	A	19700916	BE 1970-748781	19700410

NL 7005224	A	19710202	NL 1970-5224	19700410
PRIORITY APPLN. INFO.:			JP 1969-59873	A 19690729
			JP 1969-59874	A 19690729

AB A catalyst mixture containing 0.005-0.5 weight % amorphous or hexagonal GeO<sub>2</sub> [1310-53-8] or germanium tetraethoxide [14165-55-0], Sb [7440-36-0] to prevent loss of Ge (0.1-2.0 Sb per Ge; particle diameter <100-μ), Ca(OAc)<sub>2</sub> or Zn(OAc)<sub>2</sub>, and optionally containing trimethyl phosphate was useful for polycondensation of compns. containing dimethyl terephthalate (I) or mixts. of I and dimethyl isophthalate, and ethylene glycol (II) to give polyesters with improved whiteness. Thus, a mixture containing I 40, II 30, Ca(OAc)<sub>2</sub> 0.02, and Sb 0.006 g was heated at 190-210.deg. to cause ester-exchange reaction. After removal of MeOH formed the mixture was heated to 250.deg. to remove excess II. Amorphous GeO<sub>2</sub> (0.01 g) was added and the composition was heated 1 hr at 285.deg. and 0.5-mm to give a white polymer [25038-59-9], intrinsic viscosity (1:1 PhOH-C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> mixture, 25.deg.), 0.735, softening temperature 258.deg., compared to 0.624 and 251.deg., resp., for a polymer prepared from a similar composition in the absence of Sb, and 0.633 and 253.deg., resp., for a polymer prepared from a similar composition containing SbPh<sub>3</sub> instead of Sb; the proportion of GeO<sub>2</sub> retained in the product was 76%, compared to 40% for polycondensation of a similar composition without Sb.

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L1 1 JP 48038635/PN  
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L1 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1975:98831 CAPLUS Full-text

DOCUMENT NUMBER: 82:98831

TITLE: Polyester

INVENTOR(S): Chimura, Kazuchika; Ito, Kazuo; Takashima, Shunichi;  
Shindo, Tamao; Kawashima, Masao

PATENT ASSIGNEE(S): Mitsubishi Rayon Co., Ltd.

SOURCE: Jpn. Tokkyo Koho, 4 pp.

CODEN: JAXXAD

DOCUMENT TYPE: Patent

LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 2

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 48038635	B	19731119	JP 1969-59874	19690729 <--
BE 748781	A	19700916	BE 1970-748781	19700410
NL 7005224	A	19710202	NL 1970-5224	19700410
PRIORITY APPLN. INFO.:			JP 1969-59873	A 19690729
			JP 1969-59874	A 19690729

AB A catalyst mixture containing 0.005-0.2 weight % crystalline GeO<sub>2</sub> [1310-53-8] (particle diameter .apprx.100  $\mu$ ) and Ca(OAc)<sub>2</sub> [62-54-4] or CaH<sub>2</sub> [7789-78-8] (0.4-1.5 Ca per Ge) as a solution in ethylene glycol (I), Sb [7440-36-0] (0.1-2.0 Sb per Ge; particle diameter <100  $\mu$ ), and CaO, Zn(OAc)<sub>2</sub>, or Mg(OAc)<sub>2</sub>, and optionally containing triphenyl phosphate was useful for polycondensation of a composition containing dimethyl terephthalate (II) or mixts. of II and dimethyl isophthalate, and I to give polyesters with improved whiteness. Thus, a mixture containing II 200, I 150, Ca(OAc)<sub>2</sub> 0.1, and Sb 0.024 g was heated at 190-210° to cause ester-exchange reaction. After removal of MeOH formed the mixture was heated to 250° to remove excess I. A composition containing 0.04 g hexagonal GeO<sub>2</sub> and 0.04 g Ca(OAc)<sub>2</sub> in I was added and the mixture was heated 1 hr at 285° and 0.5 mm to give a white polymer [25038-59-9], intrinsic viscosity (1:1 PhOH-C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> mixture, 25°) 0.782 and softening temperature 259°, compared to 0.674 and 252°, resp., for a polymer prepared from a similar composition in the absence of Sb, and 0.688 and 254°, resp., for a polymer prepared from a similar composition containing SbPh<sub>3</sub> instead of Sb; the amount of GeO<sub>2</sub> retained in the polymer was 87%, compared to 72% for similar polymerization without Sb.

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LOGOFF? (Y)/N/HOLD:y

COST IN U.S. DOLLARS

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ENTRY	SESSION
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FULL ESTIMATED COST

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

SINCE FILE	TOTAL
ENTRY	SESSION
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STN INTERNATIONAL LOGOFF AT 15:23:58 ON 01 AUG 2007

L5 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN  
ACCESSION NUMBER: 1974:507211 CAPLUS Full-text  
DOCUMENT NUMBER: 81:107211  
TITLE: Polyester  
INVENTOR(S): Chimura, Kazuchika; Ito, Kazuo; Takashima, Shunichi;  
Shindo, Tamao; Kawashima, Masao  
PATENT ASSIGNEE(S): Mitsubishi Rayon Co., Ltd.  
SOURCE: Jpn. Tokkyo Koho, 3 pp.  
CODEN: JAXXAD  
DOCUMENT TYPE: Patent  
LANGUAGE: Japanese  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 48038637	B	19731119	JP 1969-70282	19690906 <--
BE 751435	A	19701116	BE 1970-751435	19700604
NL 7012880	A	19710309	NL 1970-12880	19700831

PRIORITY APPLN. INFO.: JP 1969-70282 A 19690906  
AB Polyethylene terephthalate [25038-59-9] having good whiteness and transparency even after spinning was prepared using Sb [7440-36-0] in the ester exchange catalyst composition. Thus, dimethyl terephthalate 1000, ethylene glycol 750, Mn(OAc)<sub>2</sub> 0.2 and Sb 0.05 part were heated 3 hr at 150-220.deg. while removing MeOH. GeO<sub>2</sub> was added after removing ethylene glycol and the mixture was heated 3 hr at 280.deg. at 1 mm to give white polymer having intrinsic viscosity 0.711.

JP 48056782

L1 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN  
ACCESSION NUMBER: 1974:438105 CAPLUS Full-text  
DOCUMENT NUMBER: 81:38105  
TITLE: Poly(alkylene terephthalate) with high softening point

INVENTOR(S): Kitamura, Kazuyuki; Okamoto, Toshio; Kimura, Yoshio  
PATENT ASSIGNEE(S): Asahi Chemical Industry Co., Ltd.  
SOURCE: Jpn. Kokai Tokkyo Koho, 8 pp.  
CODEN: JKXXAF  
DOCUMENT TYPE: Patent  
LANGUAGE: Japanese  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 48056782	A	19730809	JP 1971-93182	19711122 <--
PRIORITY APPLN. INFO.:			JP 1971-93182	A 19711122

AB The title polymers were prepared by condensing bis( $\omega$ -hydroxyalkyl) terephthalates and/or their oligomers in the presence of an addition compound of phosphorous acid [13598-36-2] or hypophosphorous acid [6303-21-5] with amines. Thus, a mixture of di-Me terephthalate 100, ethylene glycol (I) 70, and Mn(OAc) $2 \cdot 4H_2O$  0.03 part was heated at 165-210.deg. to remove the theor. amount of MeOH, mixed with 20% I soln of phosphorous acid-triethylamine (1:4) adduct [51732-17-3] (0.05 mole %), GeO $_2$  (0.015 part in I), and TiO $_2$  (0.5 part in I), and heated at 280.deg./0.1 mm for 2 hr to prepare poly(ethylene terephthalate) [25038-59-9] softening at 262.0.deg., compared with 259.0.deg. for polymer prepared with H $_3$ PO $_3$  instead of the adduct.



L4 ANSWER 1 OF 1 CAPLUS. COPYRIGHT 2007 ACS on STN  
ACCESSION NUMBER: 1974:438106 CAPLUS Full-text  
DOCUMENT NUMBER: 81:38106  
TITLE: Poly(alkylene terephthalate) with high softening point  
INVENTOR(S): Kitamura, Kazuyuki; Okamoto, Toshio; Kimura, Yoshio  
PATENT ASSIGNEE(S): Asahi Chemical Industry Co., Ltd.  
SOURCE: Jpn. Kokai Tokkyo Koho, 6 pp.  
CODEN: JKXXAF  
DOCUMENT TYPE: Patent  
LANGUAGE: Japanese  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 48056783	A	19730809	JP 1971-93183	19711122 <--
PRIORITY APPLN. INFO.:			JP 1971-93183	A 19711122

AB The title polymers were prepared by condensing bis( $\omega$ -hydroxyalkyl) terephthalates and/or their oligomers in the presence of an addition compound of phosphoric acid [7664-38-2] or polyphosphoric acid with amines. Thus, a mixture of p-(MeO<sub>2</sub>C)2C<sub>6</sub>H<sub>4</sub> 100, ethylene glycol (I) 70, and Mn(OAc)2.4H<sub>2</sub>O 0.03 part was heated at 165-210.deg. to remove the theor. amount of MeOH, and mixed with 0.05 mole % phosphoric acid-tributylamine (1:2) adduct [51732-15-1] 0.015 part GeO<sub>2</sub> in I), and 0.5 part Ti-O<sub>2</sub> (in I), and heated at 280.deg./0.1 mm for 2 hr to prepare di-Me terephthalate-ethylene glycol copolymer [25038-59-9] softening at 261.2.deg., compared with 258.5.deg. using H<sub>3</sub>PO<sub>4</sub> instead of the amine adduct.

L2 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN  
 ACCESSION NUMBER: 1974:438108 CAPLUS Full-text  
 DOCUMENT NUMBER: 81:38108  
 TITLE: Poly(alkylene terephthalate) with high softening point  
 INVENTOR(S): Kitamura, Kazuyuki; Okamoto, Toshio; Kimura, Yoshio  
 PATENT ASSIGNEE(S): Asahi Chemical Industry Co., Ltd.  
 SOURCE: Jpn. Kokai Tokkyo Koho, 10 pp.  
 CODEN: JKXXAF  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 48056784	A	19730809	JP 1971-93184	19711122 <--
PRIORITY APPLN. INFO.:			JP 1971-93184	A 19711122

AB The title polymers were prepared by condensing bis( $\omega$ -hydroxyalkyl) terephthalates and/or their oligomers in the presence of an addition compound of an acid phosphate or acid phosphite with an amine. Thus, a mixture of p-(MeO<sub>2</sub>C)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> 100, ethylene glycol (I) 70, and Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O 0.03 part was heated at 165-210.deg. to remove the theor. amount of MeOH, mixed with 0.05 mole % N,N-dibutylethanolamine-methyl acid phosphate (4:1) adduct [51732-16-2], 0.015 part GeO<sub>2</sub> (in I), and 0.5 part TiO<sub>2</sub> (in I), and heated at 280.deg./0.1 mm for 2 hr to prepare di-Me terephthalate-ethylene glycol copolymer [25038-59-9] softening at 262.5.deg., compared with 259.3.deg. when Me acid phosphate was used instead of the amine adduct.

**Patent Number(s): JP48079898-A**

**Title:** High mol-wt polyester with good whiteness - prepd by melting bis-(beta-hydroxyethyl) terephthalate quenching and finally poly condensing with a catalyst

**Patent Assignee Name(s) and Code(s):** KURARAY CO LTD (KURS-C)

**Derwent Primary Accession Number:** 1974-33336V [18]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

A mixt. of bis(beta-hydroxyethyl) terephthalate (I) having extinction coeffs. 1.70 plus-or-minus 0.30 x 10<sup>4</sup> and 1.80 plus-or-minus 0.30 x 10<sup>3</sup> l./mole-cm at 242 and 288 mu, resp., in 95% aq. EtOH and >10% 2-4C glycol is melted at >90 degrees, quenched, washed or recrystd. with H<sub>2</sub>O, hydrocarbon, halogenated hydrocarbon, alc., ether, ketone, carboxylic acid, lower alkyl carboxylate, mercaptan, and/or sulphide, dried, heated 10-120 min. at 100-290 degrees, and polycondensed in the presence of <0.1 wt.% polycondensation catalyst at high temp. and reduced pressure. The product has good whiteness and high mol. wt.

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A05-E04A; A10-G01

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP48079898-A	26 Oct 1973		197418		

**Priority Application Information and Date:**

JP010729	28 Jan 1972
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**Patent Number(s):** DE2313362-A; **JP49005918-A**; GB1418896-A; CA1006545-A

**Title:** Sepg products of olefin sulphitation - with recovery of lower alcohol used as reaction medium

**Patent Assignee Name(s) and Code(s):** UNILEVER NV (UNIL-C)

**Derwent Primary Accession Number:** 1973-64186U [43]

**Patents Cited by Inventor:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Citing Patents:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Title reaction mixt. contg. an olefin-bisulphite adduct, unreacted materials, water, a 2-4C alcohol (pref. isopropanol, and sulphite and bisulphite ions is sepd. by (1) sepg. the solid adduct from the liq. phase; (2) allowing the component of the liq. phase to separate, and removing the upper phase consisting mainly of the unreacted organic materials; (3) introducing bisulphite ions into the lower phase (pref. by adding a metabisulphite and an alkaline substance) and allowing the resulting two phases to separate, and (4) sepg. the upper phase consisting mainly of an alcohol-water mixt. from the lower phase consisting mainly of an aq. soln of the bisulphate material. By this method the 2-4C alcohol used as a reaction medium pref in mixt. with water) is recovered without distn. The whole process can be carried out continuously. The alkanesulphonates isolated by this method are used as active detergents.

**International Patent Classification:** C07C-139/00

**Derwent Class:** D25 (Detergents other than soap); E17 (Other aliphatics)

**Derwent Manual Code(s):** D11-D05; E10-A09A; E10-E04

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
DE2313362-A			197343		
<b>JP49005918-A</b>	19 Jan 1974		197412		
GB1418896-A	24 Dec 1975		197552		
CA1006545-A	08 Mar 1977		197712		

**Priority Application Information and Date:**

GB013089	21 Mar 1972
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JP 49006835

L6 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN

ACCESSION NUMBER: 1975:31774 CAPLUS Full-text

DOCUMENT NUMBER: 82:31774

TITLE: Polyesters

INVENTOR(S): Watanabe, Toru; Natsui, Kiyohisa; Kato, Takashige;  
Sasaki, Shingo; Mori, Hitokazu

PATENT ASSIGNEE(S): Japan Ester Co., Ltd.

SOURCE: Jpn. Tokkyo Koho, 3 pp.

CODEN: JAXXAD

DOCUMENT TYPE: Patent

LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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JP 49006835	B	19740216	JP 1970-92575	19701021 <--
PRIORITY APPLN. INFO.:			JP 1970-92575	19701021

AB Dimethyl terephthalate (I) is transesterified with ethylene glycol (II), and the product is polycondensed in the presence of a II dispersion of Sb2O3 [1309-64-4] as catalyst to give white polyester [25038-59-9]. Thus, a mixture of 1 kg II, 50 g Sb2O3, and 5.0 g condensate of Na naphthalenesulfonate and HCHO was stirred at 35° for 2 hr, decanted, and allowed to stand for 24 hr to give a 4.26% Sb2O3 dispersion. A mixture of 7.76 kg I, 4.96 kg II, and 1.17 g Zn(OAc)2 was transesterified 5 hr at 120-230°, treated with 2.48 g Ph3PO3 and 48 ml Sb2O3 dispersion, and polycondensed 2 hr 35 min at 280°/0.5 mm to give a white polymer with intrinsic viscosity 0.72 (1:1 PhOH-C2H2Cl4, 20°) and m.p. 256 5°

L7 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN  
ACCESSION NUMBER: 1975:18518 CAPLUS Full-text  
DOCUMENT NUMBER: 82:18518  
TITLE: Polyesters  
INVENTOR(S): Chimura, Kazutoshi; Ito, Kazuo; Takashima, Shunichi;  
Shimoshinbara, Yoshihiro; Shindo, Tamao  
PATENT ASSIGNEE(S): Mitsubishi Chemical Industries Co., Ltd.  
SOURCE: Jpn. Tokkyo Koho, 4 pp.  
CODEN: JAXXAD  
DOCUMENT TYPE: Patent  
LANGUAGE: Japanese  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 49006839	B	19740216	JP 1970-116022	19701222 <--
PRIORITY APPLN. INFO.:			JP 1970-116022	19701222

AB Polyesters with good whiteness are prepared by adding malonic acid [141-82-2] or its derivative [R1C(R2)(CO2H)2; R1, R2 = H, alkyl, cycloalkyl, aryl, allyl] to the polymerization system of bis(hydroxyethyl) terephthalate in the

presence of a Sb compound catalyst. Thus, a mixture of di-Me terephthalate 10,000, ethylene glycol 7500, and Mg(OAc)2 6 parts was transesterified, mixed at 240° with 3.2 parts tri-Me phosphate dissolved in ethylene glycol, mixed with a heated mixture of Sb2O3 [1309-64-4] 5, ethylene glycol 200, and malonic acid 3.6 parts, and polymerized 2 hr at 285°/2mm to give a white polyester with softening point 261° and intrinsic viscosity 0.757 (1:1 PhOH-CHCl2CHCl2, 25°), from which a polyester fiber with good whiteness was obtained.

L8 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN  
 ACCESSION NUMBER: 1974:507233 CAPLUS Full-text  
 DOCUMENT NUMBER: 81:107233  
 TITLE: Poly(ethylene terephthalate)  
 INVENTOR(S): Chimura, Kazuya; Ito, Kazuo; Takashima, Shunichi;  
 Shimonihiara, Yoshihiro; Shindo, Mizuo  
 PATENT ASSIGNEE(S): Mitsubishi Rayon Co., Ltd.  
 SOURCE: Jpn. Tokkyo Koho, 5 pp.  
 CODEN: JAXXAD  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 49009116	B	19740301	JP 1970-47328	19700602 <--
PRIORITY APPLN. INFO.:			JP 1970-47328	19700602

AB Polycondensation of bis( $\beta$ -hydroxyethyl) terephthalate or its mixture with isophthalate in the presence of a phosphate ester, e.g., trimethyl phosphate (I) [512-56-1], and a fused mixture containing 0.0009-0.02 mole % GeO<sub>2</sub> [1310-53-8] and .geq.0.035 mole % Sb<sub>2</sub>O<sub>3</sub> [1309-64-4] (mole ratio of Ge to Sb = .leq.0.5) based on the carboxylic acid component of the polymer formed to give polymers [containing .leq.1 weight% diethylene glycol(II) and .leq.20% Sb (based on moles of Sb in Sb<sub>2</sub>O<sub>3</sub>)] and spinning the resulting polymers gave fibers with improved brightness and dyeability. Thus, a composition containing dimethyl terephthalate 10,000, ethylene glycol(III) 7500, and Mg acetate 6 parts was heated 3 hr at 150-220.deg. under N to cause transesterification. Excess III was removed by distillation and a product prepared by heating 3.2 parts I and 100 parts III at 175.deg. and 3.2 parts 15:1 weight ratio Sb<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub> mixture were added. The mixture was polycondensed 2 hr at 285.deg./2 mm to give poly(ethylene terephthalate) (IV) [25038-59-9], intrinsic viscosity (1:1 PhOH-C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, 25.deg.) 0.761, II content 0.66%, Sb content 3% (based on moles of Sb in Sb<sub>2</sub>O<sub>3</sub>), compared to 0.626, 0.61%, and 21% for a polymer prepared similarly in the presence of Sb<sub>2</sub>O<sub>3</sub> instead of Sb<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub> mixture IV was spun to give 75 denier (36 filaments) fibers, optical brightness 88.1%, compared to 80.4% for fibers obtained from a polymer prepared similarly in the presence of Sb<sub>2</sub>O<sub>3</sub>.

**Patent Number(s): JP49010834-A**

**Title:** Chemical milling metal - by immersing in a dil aq soln of mineral acid and lignin inhibitor

**Patent Assignee Name(s) and Code(s):** ARMCO STEEL CORP (ARMC-C)

**Derwent Primary Accession Number:** 1974-25800V [14]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Method of treating stainless steel and nickel alloy, comprises Immersing in an aq. soln. of H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub>, and lignin inhibitor, removing desired amt. of metal by treating it for several hours at a temp. which causes microcoarse surface to form. no surface cracking occurs.

**Derwent Class:** M14 (Other chemical surface treatments)

**Derwent Manual Code(s):** M14-A

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP49010834-A	30 Jan 1974		197414		

**Priority Application Information and Date:**

JP053885	01 Jun 1972
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**Patent Number(s):** JP49045015-A; JP79011289-B

**Title:** Dicarboxylic acid glycol esters prepn. - by transesterification in presence of an epoxide or styrene oxide with quaternary ammonium or tert amine compds

**Patent Assignee Name(s) and Code(s):** TOYO SPINNING CO LTD (TOYM-C); TOYO SPINNING CO LT (TOYM-C); (TOYM-C)

**Derwent Primary Accession Number:** 1974-62035V [20]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Dicarboxylic acid glycol esters are prepd. by transesterification in the presence of (a) epoxide (I; X = halo, 1-10C alkyl, RO, p-R'C<sub>6</sub>H<sub>4</sub>O, where R = 1-17C alkyl and R' = 1-8C alkyl, halo, Ph) or styrene oxide and (b) quaternary ammonium salts or hydroxides. tertiary amines, their org. acid salts, phosphines, alkali or alk. earth metal salts, or M1M2R complex (M1-2 = metal, R = H, 1-4C alkyl), with or without usual ester-interchange catalysts. This effects rapid transesterification. In an example, heating 582 pts. di-me terephthalate and 410 pts. ethylene glycol with 4.5 pts. Ph glycidyl ether and 0.64 pts. cetyltrimethylammonium chloride at 197 degrees caused 98.5% transesterification in 30 min and complete reaction in 33 min. Polymn. with Sb<sub>2</sub>O<sub>3</sub> gave a colourless polyester of high intrinsic viscosity.

**International Patent Classification:** B01J-031/02; C07C-067/03; C07C-069/00

**Derwent Class:** A41 (Monomers, Condensants (see also Section E)); E19 (Other organic compounds general - unknown structure, mixtures)

**Derwent Manual Code(s):** A02-A; A05-E01A; E10-G02

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP49045015-A	27 Apr 1974		197435		
JP79011289-B	14 May 1979		197923		

**Priority Application Information and Date:**

JP089856	07 Sep 1972
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**Patent Number(s): JP49045014-A**

**Title:** Dicarboxylic acid glycol esters - prepd. by transesterification in presence of quat. ammonium halides or pyridinium halides, alkali metal hydride and other cpds

**Patent Assignee Name(s) and Code(s):** TOYO SPINNING CO LTD (TOYM-C); (TOYM-C)

**Derwent Primary Accession Number:** 1974-60632V [20]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Dicarboxylic acid glycol esters are prepd. by transesterification in the presence of (a) quaternary ammonium halides  $R_1R_2R_3R_4N^+X^-$  ( $R_1-4 = 1-23C$  alkyl,  $PhCH_2$ ,  $Ph$ ;  $X =$  halo) or pyridinium halides  $R(C_5H_5N^+)X^-$  ( $R = 1-23C$  alkyl,  $PhCH_2$   $Ph$ ) and (b) alkali metal hydrides or salts,  $M_1M_2R$  complex ( $M_1-2 =$  metal;  $R = H$ ,  $1-4C$  alkyl), phosphines, tertiary amines, or their org. acid salts, with or without usual ester-interchange catalysts. This effects rapid transesterification. In an example, heating 582 parts di-Me terephthalate and 410 parts ethylene glycol with 1.92 parts cetyltrimethyl-ammonium chloride and 0.6 part KOAc at 197 degrees caused 90.5% transesterification in 30 min and the reaction completed in 60 min, compared with 78.3% and 185 min, resp., for the control (0.21 part  $Zn(OAc)_2$ ). Polymn. with  $Sb_2O_3$  gave a colourless polyester of higher intrinsic viscosity.

**Derwent Class:** A41 (Monomers, Condensants (see also Section E)); E19 (Other organic compounds general - unknown structure, mixtures)

**Derwent Manual Code(s):** A02-A; A02-A07; A05-E01A; E10-E04

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP49045014-A	27 Apr 1974		197434		

**Priority Application Information and Date:**

JP089855	07 Sep 1972
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**Patent Number(s):** JP50039711-A; JP79037607-B

**Title:** Zinc oxide -zinc sulphide type composite ceramics - contg. small cobalt oxide content, for electroluminescent and photoelectric devices

**Patent Assignee Name(s) and Code(s):** MATSUSHITA ELEC IND CO LTD (MATU-C)

**Derwent Primary Accession Number:** 1975-69670W [42]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Ceramics composed of ZnO-based ceramic layers and Zn ZnS-based ceramic layers are prep'd. from ZnO contg. 0.01-2.5 wt.% CoO. The addn. of CoO lowers the elec. resistant of the ZnO- and ZnS-based layers, and thus, the ceramics are useful in various electronics devices e.g. electroluminescent and photoelec. devices.

**International Patent Classification:** B32B-009/00; C04B-035/00; C04B-039/00; C04B-041/06; C09K-011/22; H01L-031/12

**Derwent Class:** L03 (Electro-(in)organic, chemical features of electrical devices); P73 (Layered products); U12 (Discrete Devices, e.g. LEDs, photovoltaic cells)

**Derwent Manual Code(s):** L02-J02C; L03-C02C; L03-D04E

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP50039711-A	12 Apr 1975		197542		
JP79037607-B	16 Nov 1979		197950		

**Priority Application Information and Date:**

JP091483	14 Aug 1973
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**Patent Number(s):** JP51042795-A; JP78020077-B

**Title:** Polyester prepn. by ester-interchange, condensation polymerisation - using ethylene-glycol and dimethyl-terephthalate in specified ratio with catalyst

**Patent Assignee Name(s) and Code(s):** TORAY IND INC (TORA-C)

**Derwent Primary Accession Number:** 1976-40686X [22]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Polyester is prepd. by ester-exchanging and condens.-polymsg. a dicarboxylic acid, mainly of dimethylterephthalate, with glycol, mainly of ethyleneglycol, using a molar ratio of ethyleneglycol:dimethylterephthalate = 1.30:1-1.80:1. An ester-exchanging catalyst satisfying the equation (I) is used; the ester-exchanging reaction completed below 250 degrees C followed by condensn. polymsn.- (where  $K(\text{hr}^{-1}(\text{mol.}/\text{kg.})^{-1})$  represents the reaction velocity constant between methyl ester and hydroxyl gp. of hydroxyethyl ester; and  $m$  = molar ratio of ethyleneglycol to dimethylterephthalate.

**International Patent Classification:** C07C-067/03; C07C-069/82; C08G-063/22

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A05-E04A

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP51042795-A	12 Apr 1976		197622		
JP78020077-B	24 Jun 1978		197829		

**Priority Application Information and Date:**

JP115463	09 Oct 1974
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**Patent Number(s):** JP51127195-A; JP78037116-B

**Title:** Polyester prodn. from crude terephthalic acid and ethylene glycol - and polycondensing the obtd. ester in presence of metal cpds.

**Patent Assignee Name(s) and Code(s):** MITSUBISHI CHEM IND LTD (MITU-C)

**Derwent Primary Accession Number:** 1976-95439X [51]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Good quality polyester is produced by reacting crude terephthalic acid and ethylene glycol, and polycondensing the obtd. ester. Terephthalic acid contg. 100-1000 ppm of 4-carboxybenzaldehyde is esterified directly with ethyleneglycol. The obtd. ester is polycondensed in the presence of an antimony cpd., a cobalt cpd. and a tin cpd. The Sb cpd. may be antimony trioxide,  $0.6-4 \times 10^{-4}$  mol per mol of terephthalic acid; the Co cpd. may be cobalt chloride or cobalt acetate,  $0.5-5 \times 10^{-4}$  mol as cobalt per mol of terephthalic acid and the Sn cpd. may be tin oxide or tin succinate, 3-50 ppm as tin per terephthalic acid. Polyester is used to produce fibres and films.

**International Patent Classification:** C07C-067/08; C07C-069/82; C08G-063/36

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A02-A06; A02-A07A; A05-E04A

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP51127195-A	05 Nov 1976		197651		
JP78037116-B	06 Oct 1978		197844		

**Priority Application Information and Date:**

JP052318	30 Apr 1975
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## JP 51145594

L1 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN  
ACCESSION NUMBER: 1977:91636 CAPLUS Full-text  
DOCUMENT NUMBER: 86:91636  
TITLE: Polyester fibers having good brightness from  
terephthalic acid  
INVENTOR(S): Nakagawa, Junyo; Kondo, Yoshifumi; Tsuji, Takaakira  
PATENT ASSIGNEE(S): Kuraray Co., Ltd., Japan  
SOURCE: Jpn. Kokai Tokkyo Koho, 6 pp.  
CODEN: JKXXAF  
DOCUMENT TYPE: Patent  
LANGUAGE: Japanese  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 51145594	A	19761214	JP 1975-69866	19750610 <--
PRIORITY APPLN. INFO.:			JP 1975-69866	A 19750610

AB Terephthalic acid (I), with or without <20% isophthalic acid, and ethylene glycol (II) are heated in a reactor containing 7-40% of the product from the previous batch in the presence of 0.005-0.2 mol % (based on I) amines to 90-98.5% esterification and polycondensed in the presence of 2-200 ppm (calculated as P) P compds. to give polyester fiber materials having good brightness and containing relatively few diethylene glycol (III) units. Thus, I 100, II 67.2, Sb2O3 0.035, TiO2 0.52, and Bu3N [102-82-9] 0.0444 part were heated 168 min in a reactor containing 17% of the product from the previous batch at 250° and 1.3 kg/cm2 to 94% esterification. An 83% portion of the product was transferred to a next reactor, heated and evacuated in the presence of 0.0245 part H3PO3 to 275°/10 mm, held there for 20 min addnl., and heated 71 min at 280°/0.5 mm to give polyester (IV) having intrinsic viscosity 0.63 dL/g (30°, 1:1 PhOH-C2H2Cl4) and containing 2.2 mol % III units, which was spun into fibers having brightness (Y value) 1.1, compared with 75 min, 6.1 mol %, and 6.2, resp., for a similar IV prepared by esterifying I with II without the product from the previous batch (94% esterification time 400 min).

**Patent Number(s):** JP52123489-A

**Title:** Heat resistant polyester prodn. - using opt. halogenated organo-tin and trivalent antimony cpds.

**Patent Assignee Name(s) and Code(s):** TORAY IND INC (TORA-C)

**Derwent Primary Accession Number:** 1977-84085Y [47]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Polyesters are prepd. by polycondensation of bifunctional carboxylic acids glycol ester (I) and/or its low polymer, using trivalent antimony cpd. as the polycondensation catalyst and tetravalent tin cpd(s) of formulae (I), (II) and (III). These are added after the esterification or trans-esterification. The molar ratio of Sn/Sb is 0.005-0.1: (I) is prepd. by reacting bifunctional carboxylic acid contg. chiefly terephthalic acid, or its ester-forming deriv. with glycol, contg. chiefly ethylene glycol, or its ester-forming deriv. In the formulae R1 = 1-10C alkyl, cycloalkyl, aryl or OH; R2 and R3 = 1-10C alkyl cycloalkyl, or aryl; X and Y are halo 1-12C alkoxyl (pref. C<sub>2</sub>H<sub>5</sub>O) and Z = halogen (pref. Cl) R1-3 is pref. C<sub>4</sub>H<sub>9</sub>. Halogen is pref. Cl. The polyester has improved colour tone and heat resistance.

The trivalent antimony cpds. are antimony trioxide antimony glycolate, etc. and are used pref. in concs. of 0.03-0.1 mol% based on the acid component in the polymer.

**International Patent Classification:** C08G-063/36

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A02-A07; A02-B; A05-E01A

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP52123489-A	17 Oct 1977		197747		

**Priority Application Information and Date:**

JP039264	09 Apr 1976
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**Patent Number(s): JP52129798-A**

**Title:** Polyester prodn. esp. polyethylene terephthalate with fewer ether-gps. - by esterifying in the presence of e.g. titanium cpd. and then adding alkoxide of antimony and/or germanium and polycondensing

**Patent Assignee Name(s) and Code(s):** MITSUBISHI RAYON CO LTD (MITR-C)

**Derwent Primary Accession Number:** 1977-88839Y [50]

**Patents Cited by Inventor:** 0 **Citing Patents:** 0 **Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0 **Articles Cited by Examiner:** 0

**Abstract:**

Prodn. comprises continuously reacting a slurry of terephthalic acid contg. ethylene glycol in a molar ratio 1.05-1.8. Reaction is at 230-270 degrees C under atmospheric pressure - 7 kg/cm<sup>2</sup>-G until 80-94% of the residual gps. of acid remain. Reaction mixt is fed to a second reactor a d allowed to react at 250 degrees C-280 degrees C and atmospheric pressure -200 mmHg-ab until >95% of the residual acid gps. are esterified.

Esterification is conducted in the presence of 1 of Ti Mg and Co cpds. and then antimony alloxide and/or germanium alkoxide are added to the esterified material, followed by subjecting the whole mixture to polycondensation, to obtain the corresp. polyester.

Process is esp. for prodn. of polyethylene terephthalate contg. relatively fewer ether-linkages with high whiteness.

**International Patent Classification:** C08G-063/22

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A02-A06; A02-A07; A02-A07A; A05-E04A

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP52129798-A	31 Oct 1977		197750		

**Priority Application Information and Date:**

JP047443	26 Apr 1976
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**Patent Number(s): JP52129799-A**

**Title:** Polyester prodn. esp. polyethylene terephthalate with fewer ether gps. - by esterification in presence of e.g. cobalt cpd. and then adding alkoxide of antimony and/or germanium and polycondensing

**Patent Assignee Name(s) and Code(s):** MITSUBISHI RAYON CO LTD (MITR-C)

**Derwent Primary Accession Number:** 1977-88840Y [50]

**Patents Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Citing Patents:** 1

**Articles Cited by Inventor:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Prodn. of polyester is by esterifying terephthalic acid and ethylene glycol in two steps, continuously followed by subjecting the esterified prod. to polycondensation.

Ethylene glycol and terephthalic acid are mixed in a molar ratio of 1.2-2.0 and the mixture is made into a slurry, which is continuously fed to a first reaction vessel a part of the ethylene glycol being taken out of the bottom of the rectification tower attached to the first reaction vessel so that the molar ratio of ethylene glycol and terephthalic acid in the reaction product in the first reaction vessel is 1.0-1.3. At least part of the liquid thus removed is fed to the second reaction vessel together with the esterified product taken out of the first reaction vessel.

Esterification in the second reaction vessel is with a molar ratio ethylene glycol and terephthalic acid of 1.05-1.3. Esterification is conducted in the presence of 1 Co Mg or Ti cpd. followed by addition of antimony alkoxide and/or germanium alkoxide and polycondensation.

Process allows prodn. of polyethylene terephthalate contg. fewer ether linkages and high whiteness.

**International Patent Classification:** C08G-063/22

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A02-A06; A02-A07; A02-A07A; A05-E04A

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP52129799-A	31 Oct 1977		197750		

**Priority Application Information and Date:**

JP047444	26 Apr 1976
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**Patent Number(s): JP53051294-A**

**Title:** Polyester prodn. from terephthalic acid and ethylene glycol - using catalyst obtd. by reacting antimony cpd. and cobalt cpd. in ethylene glycol solvent

**Patent Assignee Name(s) and Code(s):** MITSUBISHI RAYON CO LTD (MITR-C)

**Derwent Primary Accession Number:** 1978-44662A [25]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Prepn. of polyester comprises esterifying terephthalic acid with ethylene glycol and polymerising the resulting ester to obtain polyester. A soln. obtd. by reacting an Sb cpd. and a Co cpd. in ethylene glycol as solvent is used as catalyst.

Esterification is carried out in a simple batch process, semi-batch process or a continuous process. The catalyst is prepd. either by mixing ethylene glycol soln. of Sb cpd. and Co cpd. to react and dissolve, or by adding Co cpd. to ethylene glycol soln. of Sb cpd. and heating to react and dissolve. The amt. of Sb cpd. in the soln. is 0.005-3.0 (1.0-2.0) wt.% in terms of Sb<sub>2</sub>O<sub>3</sub> and the amt. of Co cpd. is 0.005-4.0 (1.0-2.0) wt.% in terms of Co acetate.

The esterification rate is increased, formation of diethylene glycol as a by-prod. is inhibited and colouring of the polymer is prevented.

**International Patent Classification:** C07C-067/08; C07C-069/82; C08G-063/34

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A02-A06; A02-A07A; A05-E04A

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP53051294-A	10 May 1978		197825		

**Priority Application Information and Date:**

JP126925	22 Oct 1976
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**Patent Number(s): JP53051295-A**

**Title:** Polyester prodn. from terephthalic acid and ethylene glycol - using catalyst obtd. by reacting antimony cpd., cobalt cpd. and phosphorus cpd. in ethylene glycol solvent

**Patent Assignee Name(s) and Code(s):** MITSUBISHI RAYON CO LTD (MITR-C)

**Derwent Primary Accession Number:** 1978-44663A [25]

**Patents Cited by Inventor:** 0

**Citing Patents:** 2

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Prepn. of polyester comprises esterifying terephthalic acid wit ethylene glycol and polymerising the resulting ester to obtain polyester. A soln. obtd. by reacting an Sb cpd., a Co cpd. and a P cpd. in ethylene glycol solvent is used as catalyst.

Esterification is by a simple batch process, a semi batch process or a continuous process. The catalyst is prepd. by mixing and reacting ethylene glycol solns. of Sb cpd., Co cpd. and P cpd. by adding Co cpd. to the ethylene glycol soln of Sb cpd. to react and then adding P cpd. to the resulting soln. or by mixing the ethylene glycol solns. of Sb cpd. and of P cpd. and then adding Co cpd. to react and dissolve.

The amt. of Sb cpd. is 0.005-3.0 (1.0-2.0) wt.% in terms of Sb<sub>2</sub>O<sub>3</sub>, the amt. of Co cpd. is 0.005-4.0 (1.0-2.0) wt.% in terms of Co acetate and the amt. P cpd. is 0.001-3.0 (0.5-2.0) wt.% in terms of trimethyl phosphate.

The esterification rate is increased, formation of diethylene glycol as a by-prod. is inhibited and colouring of the resulting polymer is prevented.

**International Patent Classification:** C07C-067/08; C07C-069/82; C08G-063/34

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A02-A06; A02-A07A; A05-E04A

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP53051295-A	10 May 1978		197825		

**Priority Application Information and Date:**

JP126926	22 Oct 1976
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**Patent Number(s):** JP53052595-A; JP80027096-B

**Title:** Polyester prodn. - by polycondensing bis(beta-hydroxyethyl) terephthalate! in presence of antimony cpd. and organic tin cpd.

**Patent Assignee Name(s) and Code(s):** NIPPON ESTER CO LTD (NPEC-C)

**Derwent Primary Accession Number:** 1978-44914A [25]

**Patents Cited by Inventor:** 0 **Citing Patents:** 0 **Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0 **Articles Cited by Examiner:** 0

**Abstract:**

Polyesters are prepd. by polycondensing bis(beta-hydroxyethyl)terephthalate (I) or a compsn. contg. mainly (I) in the presence of an antimony cpd. and 0.01-0.05 mol (w.r.t. antimony cpd.) of an organic tin cpd. soluble in ethylene glycol.

Organic tin cpds. include organic stannic oxide, organic stannic hydroxide, organic tin alcoholate, organic tin glycolate, organic tin phenolate, inorganic acid salt of organic tin, etc. Antimony cpds. include antimony trioxide, antimony trichloride, antimony acetate and antimony glycolate

Reddening of polyesters is avoided while maintaining excellent transparency and colour tone.

**International Patent Classification:** C08G-063/34

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A02-A07; A05-E04A

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP53052595-A	13 May 1978		197825		
JP80027096-B	18 Jul 1980		198033		

**Priority Application Information and Date:**

JP126514	21 Oct 1976
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**Patent Number(s):** JP53105591-A; JP80030730-B

**Title:** Polyester prepn. from bis-(beta-hydroxyethyl)-terephthalate - by polycondensing in presence of antimony cpd., organo-tin cpd. and antioxidant, giving transparent prod. for film and fibre mfr.

**Patent Assignee Name(s) and Code(s):** NIPPON ESTER CO LTD (NPEC-C)

**Derwent Primary Accession Number:** 1978-75507A [42]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Prepn. of polyester comprises polycondensing bis-(beta-hydroxyethyl)terephthalate in the presence of (a) an Sb cpd. (b) an ethylene glycol-soluble organic Sn cpd. in an amt. of 0.01-0.3 mol. (calculated as Sn atom) per mol. of the Sb atom and (c) >0.01 mol. of an antioxidant per mol. of Sn atom.

Pref. (b) is a tetravalent organic Sn cpd. organic Sn oxide (e.g. dibutyl tin oxide) alkoxide (e.g. dibutyltin methoxide) hydroxide (e.g. triphenyltin hydroxide), glycoxide, phenoxide (e.g. dibutyltin diphenoxide) organic Sn inorganic acid salt (e.g. trimethyltin nitrate) organic sn carboxylic acid ester (e.g. dibutyltin maleate) or tetraalkyltin (e.g. tetrabutyltin). Pref. (c) is a phenol series (e.g. butyloxylanisole)amine (e.g. phenyl-alpha-naphthylamine) or quinone series (e.g. hydroquinone) antioxidant.

Addn. of (b) and (c) prevents the polyester from becoming reddish and imparts transparency. The polyester are useful as raw materials for fibres, films, etc.

**International Patent Classification:** C08G-063/34

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds); F01 (Threads and fibres, natural or artificial; spinning)

**Derwent Manual Code(s):** A02-A07; A05-E04A; A08-A06; F01-D04

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP53105591-A	13 Sep 1978		197842		
JP80030730-B	13 Aug 1980		198036		

**Priority Application Information and Date:**

JP020546	26 Feb 1977
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**Patent Number(s): JP54135896-A**

**Title:** Prepn. of polyester with good transparency and hue - by polycondensing bis(beta-hydroxyethyl)-terephthalate using antimony catalyst, adding organo-tin cpd. cobalt cpd. and alkali metal cpd.

**Patent Assignee Name(s) and Code(s):** NIPPON ESTER CO LTD (NPEC-C)

**Derwent Primary Accession Number:** 1979-86885B [48]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Polyester is prepd. by polycondensating bis(beta-hydroxyethyl)terephthalate using an Sb cpd. as catalyst.

The improvement comprises adding to the reaction system an organotin cpd. (e.g. dimethyltin oxide or trimethyltin chloride), a cobalt cpd. (e.g. CoCl<sub>2</sub> or cobalt acetate) and an alkali metal cpd. (e.g. hydroxide, methylate, ethylate carbonate, borate, formate, acetate or benzoate of Li, Na or K) in a ratio satisfying the formulae  $1 \times 10^{-4} A$   $10 \times 10^{-4}$ ;  $0.01 B/A$   $0.2$ ;  $0.2 \times 10^{-4} C$   $2 \times 10^{-4}$  and  $0.1 D/A$   $3$ . In the formulae, A, B, C, D = mol. of Sb, Sn, Co and alkali metal, respectively, per mol. of the acid component constituting the polyester).

Blue hue resulting from the cobalt cpd. is strengthened and a distinct blue colour can be obtd. unlike the blacky-blue colour obtd. by the use of the cobalt cpd. alone.

**International Patent Classification:** C08G-063/22

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A02-A07; A05-E04A; A08-M09

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP54135896-A	22 Oct 1979		197948	-	

**Priority Application Information and Date:**

JP043563	13 Apr 1978
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**Patent Number(s):** JP54163996-A; JP86018568-B

**Title:** Polyethylene terephthalate with improved colour - prepd. by polycondensation of bis beta-hydroxyethyl terephthalate in presence of added antimony, tin, cobalt and magnesium cpds.

**Patent Assignee Name(s) and Code(s):** NIPPON ESTER CO LTD (NPEC-C)

**Derwent Primary Accession Number:** 1980-10415C [18]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

In the prodn. of a polyester by polycondensn. of bis(beta-hydroxyethyl)terephthalate, an antimony cpd., organic tin cpd., cobalt cpd. and magnesium cpd. are added in amts. that satisfy the equations.  $1 \times 10^{-4} A$   $8 \times 10^{-4}$ ;  $0.01 B/A$  0.15;  $0.2 \times 10^{-4} C$   $1.5 \times 10^{-4}$ ; and  $0.1 D/A$  5., where A,B,C, and D are moles of Sb,Sn,Co and Mg per mole of acid component of the polyester.

Sb cpds. are Sb trioxide, acetate, trichloride, etc. The organic Sn cpds. are diemthyl tin oxide, triphenyl tin hydroxide, etc. The Co cpds. are Co chloride, acetate, etc. The Mg cpds. are Mg hydroxide, carbonate, etc.

The presence of the Mg cpd. increases the bluing effect of cobalt cpd. and yellowing of polyester is controlled. The method produces PET with excellent transparency and colour tone can be obtd.

**International Patent Classification:** C08G-063/36

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds); E12 (Organometallics); A60 (Additives, Compounding Agents); E37 (Mixtures of many components)

**Derwent Manual Code(s):** A02-A06; A05-E04A; A09-A02; E05-F01; E05-J; E05-L02; E31-M; E34-B; E35-V

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP54163996-A	27 Dec 1979		198006		
JP86018568-B	13 May 1986		198623		

**Priority Application Information and Date:**

JP072781	16 Jun 1978
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**Patent Number(s): JP55089332-A**

**Title:** Prod'n. of polyester having excellent properties - from terephthalic acid and glycol with addn. of phosphorus cpd. and using antimony cpd. catalyst

**Patent Assignee Name(s) and Code(s):** NIPPON ESTER CO LTD (NPEC-C)

**Derwent Primary Accession Number:** 1980-59294C [34]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

In the prepn. of polyester where difunctional carboxylic acids mainly comprising terephthalic acid and glycol are directly esterified followed by polycondensation, the improvement comprises adding a P cpd. of formula (I), pref. (II), (III) or (IV), in an amt. of  $0.2 \times 10^{-4}$  mol- $20 \times 10^{-4}$  mol per mol of the starting acid components to the esterification system and using an Sb cpd. (e.g. trioxide, trichloride or acetate) as catalyst for polycondensation. (Where n = 1 or 2; R' is H or hydrocarbon gp.; R2 is hydrocarbon gp.; R3 is H or hydrocarbon gp.).

The resulting polyester has excellent heat stability, transparency and hue. When the phosphorus cpd. is added after the completion of esterification, no improvement is obtd. The Sb cpd. is pref. used in an amt. of  $1 \times 10^{-4}$  -  $10 \times 10^{-4}$  mol (as Sb) per mol of the acid components constituting the polyester.

**Drawing:**

**International Patent Classification:** C08G-063/68

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A02-A07; A02-A11; A05-E04A

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP55089332-A	05 Jul 1980		198034		

**Priority Application Information and Date:**

JP135360	02 Nov 1978
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**Patent Number(s): JP55149320-A**

**Title:** Mfr. of polyester contg. no insoluble catalyst contaminants - using glycol soluble molybdenum, antimony titanium, tin, germanium and zinc cpds. as catalysts

**Patent Assignee Name(s) and Code(s):** NIPPON ESTER CO LTD (NPEC-C)

**Derwent Primary Accession Number:** 1981-04926D [08]

**Patents Cited by Inventor:** 0

**Citing Patents:** 2

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Process comprises using glycol soluble cpds. at least 1 of antimony, titanium, germanium, tin, zinc as catalyst and also 0.1-10 micro moles/ mol of monomer acid a glycol soluble molybdenum cpd. The dicarboxylic acid is mainly terephthalic and the glycol mainly ethylene glycol. The glycol soluble cpds. are e.g. antimony trioxide, antimony trichloride, titanium tetramethoxide, titanium tetraethoxide, germanium, tetraethoxide, germanium tetra-n-butoxide, di-n-butyl tin dichloride, tri-n-butyl tin acetate, zinc formate, zinc acetate, etc. The glycol soluble molybdenum cpd. is e.g. molybdic acid, lithium molybdate, etc.

The rate of reaction is increased considerably as if a large amt. of conventional catalyst had been used. Polymer with good quality is obtd., contg. almost no insoluble catalyst deposits.

**International Patent Classification:** C08G-063/34

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A02-A06; A02-A07; A05-E01A

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP55149320-A	20 Nov 1980		198104		

**Application Details and Date:**

JP55149320-A	JP056589	09 May 1979
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**Priority Application Information and Date:**

JP056589	09 May 1979
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**Patent Number(s): JP56008431-A**

**Title:** Polyester prodn. - from terephthalic acid, ethylene glycol, an antimony, titanium, germanium, tin, zinc, or cobalt cpd. as catalyst and a rhenium cpd.

**Patent Assignee Name(s) and Code(s):** NIPPON ESTER CO LTD (NPEC-C)

**Derwent Primary Accession Number:** 1981-20317D [12]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Polyester is produced from (1) terephthalic acid or a bifunctional carboxylic acid comprising mainly terephthalic acid or an ester-forming deriv., (2) ethylene glycol or a glycol component comprising mainly ethylene glycol, (3) one or more cpds. selected from glycol-soluble cpds. of Sb, Ti, Ge, Sn, Zn and Co as catalyst, (4) glycol-soluble rhenium cpd. in an amt. of  $0.005 \times 10^4$  to  $0.1 \times 10^4$  mole to 1 mole of the acid component constituting the polyester.

(3) is e.g.  $\text{SbO}_3$ ,  $\text{Ti}(\text{OCH}_3)_4$ , ethylgermane, di-n-butyl tin diacetate, cobalt chloride,  $\text{ZnCO}_3$ . (4) is e.g. rhenium chloride, rhenium bromide. (3) and (4) are added to the reaction system at any time by the initial stage of the polycondensn.

High polymerisation degree polymers are produced in a short time without causing deposition of insoluble matter and deterioration of colour tone.

**International Patent Classification:** C08G-063/34

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A02-A06; A05-E04A

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP56008431-A	28 Jan 1981		198112		

**Priority Application Information and Date:**

JP084220	03 Jul 1979
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# JP 57038609

L9 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2007 ACS on STN  
 ACCESSION NUMBER: 1983:90120 CAPLUS Full-text  
 DOCUMENT NUMBER: 98:90120  
 TITLE: Poly(ethylene terephthalate) with high molecular weight  
 PATENT ASSIGNEE(S): Teijin Ltd., Japan  
 SOURCE: Jpn. Tokkyo Koho, 5 pp.  
 CODEN: JAXXAD  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 57038609	B	19820817	JP 1973-56282	19730522 <--
PRIORITY APPLN. INFO.:			JP 1973-56282	19730522

AB Polymerization of bis(hydroxyalkyl) terephthalate is accelerated by adding di-Ph terephthalate (I) [1539-04-4] to the reaction mixture in the final stage of polymerization, sep. collecting the distillate containing phenol [108-95-2] after the I addition, and cleaning the distillation systems with PhOH solvents. Thus, transesterified product from di-Me terephthalate 194, ethylene glycol (II) 130, and Ca(OAc)<sub>2</sub> 0.176 part was heated 15 min in the presence of 0.88 part Sb<sub>2</sub>O<sub>3</sub> and 0.082 part H<sub>3</sub>PO<sub>3</sub> at 240-260°, heated 45 min at 260-275° and 3-760 mm, and heated 90 min at 275-280° and 0.3-3 mm recovering II (total 62 parts). I (1.9 parts) was added to the reaction mixture which was heated 60 min addnl. at 275-280° and 0.5 mm, recovering PhOH containing II in a sep. tank (0.8 parts of 24:76 PhOH-II). The reaction system was pressurized to discharge polymer [25038-59-9] having intrinsic viscosity 0.94, and the distillation system was washed with 340 parts 3:97 PhOH-I mixture, 340 parts 0.15:99.85 PhOH-I mixture, and 340 parts 0.075:99.925 PhOH-I mixture in that order.

**Patent Number(s):** JP58109532-A; JP90006769-B

**Title:** Polyester prodn. esp. from terephthalic acid and ethylene glycol - in presence of organic poly:magnesio-siloxane!

**Patent Assignee Name(s) and Code(s):** NIPPON ESTER CO LTD (NPEC-C)

**Derwent Primary Accession Number:** 1983-731268 [32]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Polyesters are produced from (1) terephthalic acid or bifunctional carboxylic acids comprising mainly terephthalic acid, or ester-forming cpds. derived from them, and (2) ethylene glycol or glycol component comprising mainly ethylene glycol or ester-forming cpds. derived from them in the presence of (3) organic polymagnesiosiloxane.

Polyesters of high polymerisation degrees and excellent colour tone are produced in a short period of time.

Component (3) is produced, e.g. by heating dihalosilane and magnesium hydroxide in ether solvent in a stream of nitrogen. Amt. of (3) added is 0.01-10 pts.wt. per 100 pts.wt. polyester formed. The target polyester is produced e.g. by ester-exchanging dimethyl terephthalate and ethylene glycol or esterifying terephthalic acid and ethylene glycol, and polycondensing bis-(beta-hydroxyethyl) terephthalate and/or its low polymer in the presence of catalyst, e.g. antimony cpd., titanium cpd., tin cpd., pref. antimony trioxide. Pref. polyesters have limiting viscosity of 0.4-1.2 (calculated from the soln. viscosity determined in phenol-ethane tetrachloride solvent at 20 deg.C.

**Drawing:**

**International Patent Classification:** C08G-063/22

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

**Derwent Manual Code(s):** A02-B; A05-E04A; A06-A00E2; A06-D; A12-W11B

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
JP58109532-A	29 Jun 1983		198332	Pages: 4	
JP90006769-B	13 Feb 1990		199010		

**Application Details and Date:**

JP58109532-A	JP211791	24 Dec 1981
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**Priority Application Information and Date:**

JP211791	24 Dec 1981
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**Patent Number(s):** EP103867-A; JP59051294-A; **JP59051295-A**; EP103867-B; DE3368418-G; US4677125-A; JP91039077-B; JP91039078-B

**Title:** Antihypertensive with angiotensin converting enzyme inhibiting action - comprises N-N'-substd.-L-iso:leucyl o-substd. -l-tyrosyl 1-amino 2-substd. ethyl:phosphonic acid, salts and ester(s)

**Inventor(s):** TERANISHI M, TAKAHASHI M, NOMOTO H, KASE H, SHUTO K, KUBO K, KARASAWA A

**Patent Assignee Name(s) and Code(s):** KYOWA HAKKO KOGYO KK (KYOW-C)

**Derwent Primary Accession Number:** 1984-083590 [14]

**Patents Cited by Inventor:** 0

**Citing Patents:** 3

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 42

**Articles Cited by Examiner:** 0

**Abstract:**

Cpds. of formula (I) and their salts are new.

R1 is H, lower alkyl, lower alkoxy carbonyl, aralkyloxycarbonyl or R6-CO-; R2 is H, lower alkyl (opt. substd. by NH2, SH, lower alkyl-thio, carboxyl, OH, guanidino or imidazolyl), aryl (opt. substd. by NH2, OH, lower alkoxy, aralkyloxy, lower alkyl, halo or NO2), aralkyl (opt. substd. by NH2, lower alkyl, halo or NO2) or -CH2-Ph-OR7; R3 is H, lower alkyl, aralkyl (opt. substd. by R6), R8-CO-, R9-O-CO- or R9NHCO-; R4 and R5 are each H, 1-18C alkyl, (opt. substd. by R6), aralkyl (opt. substd. by R6), -(CH2CH2O)mCH3 or CH(CH2OCO(CH2)nCH3)2; R6 is H, 1-17C alkyl, aryl or aralkyl (both opt. substd. by lower alkyl, lower alkoxy or halo), e.g. 5-6C cycloalkyl; R7 is the same as R3; R8 is the same as R6; R9 is lower alkyl, or aryl or aralkyl (both opt. substd. by R6); m is 1-4; and n is 0-10.

(I) show angiotensin converting enzyme inhibiting activity and are useful as antihypertensive agents.

**Drawing:**

**International Patent Classification:** A61K-031/66; A61K-037/02; C07C-103/52; C07F-009/38; C07K-005/06

**Derwent Class:** B05 (Other organics - aromatics, aliphatic, organo-metallics.)

**Derwent Manual Code(s):** B05-B01E; B05-B01F; B12-F05; B12-G01

**Patent Details:**

Patent Number	Publ. Date	Main IPC	Week	Page Count	Language
EP103867-A	28 Mar 1984		198414	Pages: 56	
JP59051294-A	24 Mar 1984		198418		
<b>JP59051295-A</b>	24 Mar 1984		198418		
EP103867-B	17 Dec 1986		198651		
DE3368418-G	29 Jan 1987		198705		
US4677125-A	30 Jun 1987		198728		
JP91039077-B	12 Jun 1991		199127		
JP91039078-B	12 Jun 1991		199127		

**Application Details and Date:**

EP103867-A	EP109190	16 Sep 1983
JP59051294-A	JP161788	17 Sep 1982
<b>JP59051295-A</b>	JP161789	17 Sep 1982
US4677125-A	US902109	29 Aug 1986
JP91039077-B	JP161788	17 Sep 1982
JP91039078-B	JP161789	17 Sep 1982

**Priority Application Information and Date:**

JP161788	17 Sep 1982
JP161789	17 Sep 1982



## **Technical Language Service**

Translations From And Into Any Language

### **JAPANESE / ENGLISH TRANSLATION OF**

**Japanese Patent Application JP 60 - 219226 A**

**Process for the Production of a Polyester  
with a High Degree of Polymerization**

**Your Ref: 081203-23**

**For: Eastman Chemical Company**

9109 Eagle Hills Dr . Las Vegas NV 89134 . ph: 866-722-7990 (toll-free) . fax: 702-973-6009 . email: sales@tls-translations.com

(19) Japanese Patent Office (JP)

(11) Unexamined Patent  
Application (Kokai) No.

(12) Unexamined Patent Gazette (A)

Sho 60-219226

(51) Int. Cl. <sup>4</sup>	Classification Symbols	Internal Office Registration Nos.	(43) Date of Publication: November 1, 1985
C 08 G	63/38	6537-4J	
	63/22	6537-4J	
Request for Examination: Not yet submitted		Number of Inventions: 1	Total of 3 pages [in original]

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- (54) Title of the Invention: **Process for the Production of a Polyester with a High Degree of Polymerization**
- (21) Application No.: Sho 59-76158
- (22) Date of Filing: April 16, 1984
- (72) Inventor: Tetsuo Matsumoto  
49-6 Kutsuichiba  
Yamato-cho, Okazaki-shi
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**SPECIFICATION**

**1. Title of the Invention**

Process for the Production of a Polyester with a High Degree of Polymerization

**2. Claims**

1. A process for the production of a polyester wherein terephthalic acid, a bifunctional carboxylic acid having terephthalic acid as the main component thereof, or an ester-forming derivative thereof is reacted with ethylene glycol, a glycol having ethylene glycol as the principal component thereof, or an ester-forming derivative to produce a polyester, said method characterized by adding hydrogen chloride in a proportion of  $0.2 \times 10^{-4} - 30 \times 10^{-4}$  mol per mole



of the raw material acid component after having substantially completed the esterification or transesterification reaction.

### 3. Detailed Description of the Invention

#### (Field of Industrial Utilization)

The present invention relates to a process for the production of a polyester; in particular, to a process for rapidly producing a polyester that has a high degree of polymerization and excellent mechanical and thermal properties.

#### (Prior Art)

Polyesters, especially polyethylene terephthalate and polyesters having ethylene terephthalate units as the main structural units, are widely used in common practice for fibers, films, and other molded articles because of their many excellent properties.

In the manufacture of polyethylene terephthalate, bis-( $\beta$ -hydroxyethyl)terephthalate and/or a low-polymer thereof is usually formed by transesterifying dimethyl terephthalate and ethylene glycol or by directly esterifying terephthalic acid and ethylene glycol, and a polyester of the desired properties is then produced by conducting a polycondensation reaction.

However, since the polycondensation step, especially the final polycondensation step, must be conducted at a high temperature of from 280 to 300°C for a long period of time in order to obtain a polyester with an intrinsic viscosity of, for example, 0.6 or higher, the polymer usually turns yellow as a result of thermal decomposition and other secondary reactions, and the increases in the concentration of terminal carboxyl groups and in the content of diethylene glycol bonds have an adverse effect on the physical properties of the polyester.

A catalyst is generally used in the manufacture of polyester. For example, Japanese Kokoku Patent No. Sho 28-4640 mentions the use of hydrogen chloride as an esterification catalyst. However, when hydrogen chloride is added from the time of the esterification reaction, the content of diethylene glycol bonds increases as a result of secondary reactions, its activity as a polycondensation catalyst declines in the extreme, and it becomes impossible to shorten the polycondensation reaction time.

### **(Object of the Invention)**

The object of the present invention is to provide a process for rapidly producing a polyester that has a high degree of polymerization and excellent mechanical and thermal properties.

### **(Constitution of the Invention)**

As a result of research intended to attain the aforementioned object, the present inventors discovered that it is effective to add a prescribed quantity of hydrogen chloride at a prescribed time, and perfected the present invention. In essence, the invention is as follows.

A process for the production of a polyester wherein terephthalic acid, a bifunctional carboxylic acid having terephthalic acid as the main component thereof, or an ester-forming derivative thereof is reacted with ethylene glycol, a glycol having ethylene glycol as the principal component thereof, or an ester-forming derivative to produce a polyester, this method characterized by adding hydrogen chloride in a proportion of  $0.2 \times 10^{-4} - 30 \times 10^{-4}$  mol per mole of the raw material acid component after having substantially completed the esterification or transesterification reaction.

The hydrogen chloride in the present invention must be added after the esterification or transesterification reaction has been substantially completed, i.e., when the rate of reaction has reached 90% or higher, and ideally 92-98%. Addition prior to this time causes problems such as those mentioned above.

The amount of hydrogen chloride added must be a proportion of  $0.2 \times 10^{-4} - 30 \times 10^{-4}$  mol per mole of the acid component, which is a starting material for the production of the polyester. The addition has essentially no effect when the amount added is lower than this range. Not only does the effect of addition reach saturation, but the polycondensation reaction is also delayed, ordinary stainless steel reactors undergo corrosion, and a special reactor such as a ceramic reactor must be used when the amount added is higher than this range.

The principal acid component in the present invention is terephthalic acid or an ester-forming derivative thereof, such as an alkyl ester or phenyl ester. Part of the acid component (usually less than 30 mol%) may be replaced with one or more compounds selected from among

methyl terephthalic acid, isophthalic acid, methyl isophthalic acid, 5-sodium sulfoisophthalic acid, phthalic acid, diphenyl dicarboxylic acid, diphenylsulfone dicarboxylic acid, diphenoxyethane dicarboxylic acid, naphthalenedicarboxylic acid, adipic acid, sebacic acid, p-hydroxyethoxybenzoic acid, ester-forming derivatives thereof, and the like. On the other hand, the principal glycol component is ethylene glycol or an ester-forming derivative of ethylene glycol, such as ethylene oxide. Part of the glycol component (usually less than 30 mol%) may be replaced by one or more compounds selected from among aliphatic, aromatic, alicyclic, and other diol compounds, such as propylene glycol, tetramethylene glycol, 1,4-cyclohexanedimethanol, 1,4-cyclohexanediol, 1,4-bis-hydroxyethoxy benzene, ester-forming derivatives thereof, and the like.

Any known method can be used to manufacture a polyester from these bifunctional carboxylic acids and glycols. For example, the prescribed properties can be obtained by a method in which bis-( $\beta$ -hydroxyethyl)terephthalate and/or a low-polymer thereof is formed by transesterifying dimethyl terephthalate and ethylene glycol, directly esterifying terephthalic acid and ethylene glycol, or carrying out an addition reaction of terephthalic acid and ethylene oxide, and in which a polycondensation reaction is then conducted by adding a prescribed quantity of hydrogen chloride. Additives such as catalysts, stabilizers, pigments, dyes, fluorescent whiteners, nucleating agents, polymerization accelerators, lubricants, and bulking agents can be introduced as needed in addition to the hydrogen chloride catalyst after the transesterification or esterification reaction has been substantially completed.

The degree of polymerization of the polyester produced is not especially restricted, but the intrinsic viscosity (abbreviated hereinafter as  $[\eta]$ ) is preferably in the range of 0.6-1.0 because of practical considerations, as determined based on the solution viscosity measured at 20°C after the polyester is dissolved in a mixed solution of phenol and tetrachloroethane (1:1).

The polyester can be manufactured in accordance with the present invention without adding any additives other than the hydrogen chloride catalyst, and a pure polyester devoid of any catalyst residue or the like can be obtained by thoroughly scattering the residual hydrogen chloride in the polyester by extended hot-air drying or vacuum drying at a temperature higher than the usual drying temperature (about 140°C), i.e., usually 160-220°C, and preferably

180-200°C. In addition, the thermal decomposition rate and the decrease in the degree of polymerization are minimized.

### **(Working Examples)**

The present invention is explained concretely below through working examples. However, the present invention is in no way limited by these working examples.

In the working examples, "parts" means "parts by weight," and the characteristics were measured as follows.

(a) The terminal carboxyl group concentration (COOH) was determined by titration with 1/10N potassium hydroxide solution in benzyl alcohol. A lower value is preferred.

(b) The concentration of diethylene glycol bonds (DEG) was determined by a method in which decomposition was performed for two hours under methanol reflux, and an analysis was conducted by gas chromatography. A lower value is usually preferred.

### **Working Examples and Comparative Examples**

Bis( $\beta$ -hydroxyethyl)terephthalate and low polymers thereof were produced from terephthalic acid and ethylene glycol by a known method. The quantities of hydrogen chloride shown in Table 1 [amount of HCl (mol) per mole of acid component] were added to 100 parts of the above, the temperature was raised to 285°C, the interior of the system was gradually evacuated, and polycondensation was finally carried out at 0.1 mm Hg for the length of time shown in Table 1.

Polyester was also produced in the same way using antimony trioxide in an amount of  $2 \times 10^{-4}$  mol/mol of acid component instead of the hydrogen chloride as the catalyst (reference example).

Table 1 shows the characteristics of the polyesters obtained.

Table 1

	Polycondensation time (min)	Amount of catalyst added		Properties of polyester produced		
		HCl (mol)	(parts)	$[\eta]$	DEG (mol%)	COOH (Eq/ton)
Working example 1	120	$10 \times 10^{-4}$	0.055	0.88	1.67	18.3
Working example 2	180	$2 \times 10^{-4}$	0.011	1.00	2.24	16.7
Comparative example 1	120	$0.1 \times 10^{-4}$	0.006	0.19	1.94	68.4
Comparative example 2	120	$40 \times 10^{-4}$	0.22	0.78	3.77	19.2
Comparative example 3	120	$70 \times 10^{-4}$	0.35	0.46	4.32	14.6
Reference example	120	—	—	0.68	1.85	15.0

Furthermore, the amount of residual hydrogen chloride in the dry polyester obtained in Working Example 1 was below the limit of detection (30 ppm) by fluorescence x-ray analysis.

The degree of polymerization did not increase and the stainless steel reactor was severely corroded in Comparative Example 3, where a large amount of hydrogen chloride was added.

#### (Merits of the Invention)

As has been described above, the method of the present invention makes it possible to manufacture polyester with a high degree of polymerization and excellent mechanical and thermal properties in a short time. In particular, it is possible to prevent increases in the content of terminal carboxyl groups and diethylene glycol bonds in the polyester produced in the treatment step that accompanies or follows the polycondensation reaction, and to greatly improve product quality when the polyester is used for fibers, films, and other molded articles.

It is also possible to obtain pure polyester that contains no catalyst residues or the like if the polyester is manufactured without adding any additives other than hydrogen chloride.

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## **Technical Language Service**

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### **JAPANESE / ENGLISH TRANSLATION OF**

**Japanese Patent Application JP 62 - 297318 A**

**Method for the Production of an Ultra-High Molecular  
Weight Polyester**

**Your Ref: 081203-15**

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(54) Title of the Invention: **Method for the Production of an Ultra-High Molecular Weight Polyester**

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SPECIFICATION**1. Title of the Invention**

Method for the Production of an Ultra-High Molecular Weight Polyester

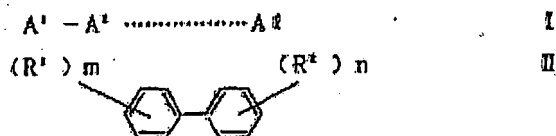
**2. Claims**

(1) A method for the production of an ultra-high molecular weight polyester,  
characterized in comprising esterification or ester exchange of a glycol and an aromatic



dicarboxylic acid or an alkyl ester thereof; and polycondensation in a heating medium in the presence of a tin compound.

(2) The method for the production of an ultra-high molecular weight polyester according to claim (1), wherein the heating medium is one or two or more compounds selected from compounds represented by the following general formulas I and II:



[In the formulas,  $A^1$  and  $A^l$  are phenyl groups or cycloalkyl groups with 5 to 20 carbons,  $A^2$  to  $A^{l-1}$  are each a phenylene group or a cycloalkylene group with 5 to 20 carbons,  $R^1$  and  $R^2$  are hydrogen atoms or alkyl groups with 1 to 20 carbons,  $l$  is an integer of 2 to 5, and  $n$  and  $m$  are integers of 0 to 5.]

(3) The method for the production of an ultra-high molecular weight polyester according to claim (1), characterized in that the polycondensation temperature is 235 to 250°C.

(4) The method for the production of an ultra-high molecular weight polyester according to claim (1), characterized in that the polycondensation is performed while inert gas is blown into the system.

(5) The method for the production of an ultra-high molecular weight polyester according to claim (1), characterized in that the polycondensation is performed while a new heating medium is being added and the byproducts are being discharged from the other end.

### 3. Detailed Description of the Invention

#### (Field of Industrial Utilization)

The present invention relates to a method for the production of an ultra-high molecular weight polyester. More particularly, it relates to a method for the production of an ultra-high molecular weight polyester from a glycol and an aromatic dicarboxylic acid or an alkyl ester thereof, wherein polycondensation is performed using a specific catalyst in a heating medium.

### **(Prior Art)**

Polyester is usually produced by a process in which an aromatic dicarboxylic acid and a glycol are subjected to direct esterification, or a glycol and an alkyl ester of an aromatic dicarboxylic acid are subjected to ester exchange, to obtain a glycol ester and/or a low polymer thereof, and the product is polycondensed by heating and agitation under a high vacuum.

### **(Problems That the Invention Is Intended to Solve)**

The method of polycondensation by heating and agitation under a high vacuum is currently used on a wide scale in commercial applications, but the method requires vacuum equipment in order to maintain a high vacuum, and strong motive power is needed to agitate highly viscous matter.

Moreover, better physical properties are required of industrial materials such as tire cords, and high molecular weight polyester is therefore being used. It is difficult to agitate this type of higher molecular weight polyester, so the method is usually used whereby the polymer after melt polycondensation is further subjected to solid phase polymerization for a long period of time in an inert gas current. Nevertheless, only a product with a limiting viscosity of 1.0 to 1.5 is usually obtained by this method.

On the other hand, it is also reported that when a polymer is crushed to a fine powder and subjected to solid phase polymerization in an inert gas ambient atmosphere, polyester with a molecular weight of as much as 120,000 is obtained (*Cryogenic Properties of Polymers*, 249, Dekker). It is cited that in this case, the polymer is partially insoluble in the solvent used for viscosity determination, and it is estimated that the molecular weight apparently increases as a result of crosslinking.

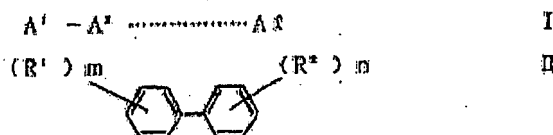
Moreover, a method whereby polyester is polymerized in a solution is cited in USP 2,597,643. However, in this case, the polymerization is performed with the polyester in the form of a completely dissolved solution. This is completely different from the present invention, in which polymerization is performed in a heating medium in which the polyester will swell but

will not dissolve. Furthermore, only polyester with a low limiting viscosity of 0.4 to 0.7 is obtained.

### (Means Used to Solve the Above-Mentioned Problems)

The inventors performed intense research in order to solve the above-mentioned problems, and ultimately perfected the present invention as a result of completely revising the prior art. That is, the present invention is a method for the production of an ultra-high molecular weight polyester characterized in comprising esterification or ester exchange of a glycol and an aromatic dicarboxylic acid or an alkyl ester thereof, and polycondensation in a heating medium in the presence of a tin compound.

As used herein, the term "heating medium" refers to an organic compound that is stable in the presence of heat and can be handled as a fluid at the reaction temperature. The heating medium can be a compound or composition selected from aromatic hydrocarbons, aliphatic hydrocarbons, alicyclic hydrocarbons, and aromatic ethers, and the like. However, in the present invention it is preferably a heating medium in which polyester will swell but not dissolve. Preferred examples include one or two or more compounds represented by the following general formulas I and II, particularly triethyl biphenyl, tetraethyl biphenyl, tripropyl biphenyl, diethyl biphenyl, trimethyl biphenyl, cyclohexylbenzene, hydrogenated biphenyl, hydrogenated terphenyl, hydrogenated triphenyl, and the like. It should be noted that the above-mentioned heating medium may also be used after being purified by a conventional method such as distillation or the like.



[In the formulas,  $A^1$  and  $A^l$  are phenyl groups or cycloalkyl groups with 5 to 20 carbons,  $A^2$  to  $A^{l-1}$  are each a phenylene group or a cycloalkylene group with 5 to 20 carbons,  $R^1$  and  $R^2$  are hydrogen atoms or alkyl groups with 1 to 20 carbons,  $l$  is an integer of 2 to 5, and  $n$  and  $m$  are integers of 0 to 5.]

Terephthalic acid, isophthalic acid, p- $\beta$ -oxyethoxybenzoic acid, 2,6-naphthalenedicarboxylic acid, 4,4'-dicarboxyldiphenyl, 4,4'-dicarboxylbenzophenone, bis(4-carboxyphenyl)ethane, 5-sodium sulfoisophthalic acid, and their alkyl esters such as methyl, ethyl, and propyl esters can be cited as examples of the aromatic dicarboxylic acids or their alkyl esters that are used in the present invention. Ethylene glycol, propylene glycol, butanediol, neopentyl glycol, diethylene glycol, cyclohexane dimethanol, ethylene oxide adducts of bisphenol A, and the like can be cited as examples of suitable glycols.

The tin compound used in the present invention is one that is soluble in polyester. Tin oxides such as stannous oxide and stannic oxide; tin halides such as stannous chloride, stannic chloride, stannous bromide, and stannic bromide; hydrates thereof; and organotin compounds such as di-n-butyltin dichloride, di-n-butyltin oxide, stannous acetate, stannous oxalate, and stannous phosphate can be cited as examples.

In addition, conventional catalysts such as antimony, titanium, germanium, cobalt, manganese, or tungsten compounds can be used together with the above-mentioned tin compound in the present invention.

The polyester production method of the present invention is described below in specific terms. An oligomer is obtained by the esterification or ester exchange of a glycol and an aromatic dicarboxylic acid or its alkyl ester by a conventional method, and then a polyester is obtained by heating and agitating this oligomer (either directly or after initial condensation) for approximately 1 to 20 hours at approximately 200 to 300°C (preferably 235 to 250°C) under normal, reduced, or increased pressure and in the presence of a heating medium and a tin compound. During the reaction, an inert gas (such as nitrogen gas, carbon dioxide gas, helium gas, or argon gas) is blown into the reaction system, and the glycol byproduct that has migrated to the heating medium is removed with by means of the inert gas or by being replaced with a new heating medium.

It should be noted that the polycondensation is performed while the oligomer or polymer in the heating medium is either in a molten state or in a solid state, depending on the heating temperature.

### (Operation of the Invention)

Operation of the present invention is as follows. That is, polycondensation of polyester is a reaction that is in equilibrium with the glycol byproduct, and a high molecular weight polymer will not be obtained unless the glycol byproduct is removed from the polymer system. It is believed that the heating medium partially impregnates the polymer and causes it to swell, and that polycondensation is promoted by eliminating the glycol byproduct from the polymer. No explanation has yet been found concerning the unique behavior of the tin compound as a catalyst.

### (Working Examples)

The present invention will now be described in specific terms with examples, but the present invention is not limited to these examples.

#### Working Example 1

Direct esterification of terephthalic acid and ethylene glycol was performed in a reaction vessel with a capacity of 500 mL that was fitted with an agitator with turbine-shaped blades, an inert gas inlet, a gas exhaust outlet, and a bottom discharge port. Then the excess ethylene glycol was removed, and 5 g of the resulting oligomer (containing, as a polymerization catalyst, 0.05 mol% stannous acetate in terms of tin in relation to the acid component; and having a limiting viscosity of 0.34, as determined at 30°C in a phenol/tetrachloroethane 6/4 mixed solvent) and 200 mL of hydrogenated triphenyl as a heating medium were introduced into the reaction vessel and agitated while being kept in a molten state by raising temperature to 240°C as nitrogen gas was blown into the reaction system at 2.0 L/min. Exhaust gas, some of the heating medium, and the ethylene glycol byproduct were discharged from the exhaust outlet, and a new heating medium was added to keep the liquid level constant at this time.

Eight hours later, the polyethylene terephthalate was removed, thoroughly washed with acetone, and dried. The polyester that was obtained was white and had a limiting viscosity of 3.0.

It should be noted that the limiting viscosity referred to in the present invention is the value determined by the following method.

The limiting viscosity, as measured at 30°C using a mixed solvent of p-chlorophenol/tetrachloroethane (3/1), was converted to phenol/tetrachloroethane (6/4) by using the following formula.

$$[\eta]_{60/40 \text{ phenol/TCE}} = 0.8352 \cdot [\eta]_{3/1 \text{ PCP/TCE}} + 0.005$$

Next, the polymer that had deposited on the inside of the reaction vessel was dissolved with 200 mL of m-cresol (it uniformly dissolved with no insoluble matter, and there was no gelling), reprecipitated, washed with methanol, and dried. The limiting viscosity of the polyester that was obtained was 3.0.

#### Working Example 2

After direct esterification of terephthalic acid and ethylene glycol using the same reaction vessel as in Example 1, conventional melt polymerization was performed. Fifty grams of the resulting oligomer (containing, as a polymerization catalyst, 0.025 mol% stannous acetate in terms of tin in relation to the acid component; and having a limiting viscosity of 0.35) and 250 mL of hydrogenated triphenyl as a heating medium were introduced into the reaction vessel, and the oligomer was directly heated and agitated in a solid phase state while being kept at 237°C by gradually raising the temperature as nitrogen gas was being blown into the reaction system at 2.0 L/minute. The exhaust gas, part of the heating medium, and the ethylene glycol byproduct were discharged from the exhaust outlet during the reaction, and a new heating medium was added to keep the liquid level constant at that time. Twelve hours later, the polyethylene terephthalate was removed, thoroughly washed with acetone, and dried. The polyester that was obtained was pale yellow and had a limiting viscosity of 3.03.

#### Working Example 3

When exactly the same method as in Working Example 2 was performed with the exception that triethyl biphenyl was used as the heating medium, the limiting viscosity of the polyester that was obtained 12 hours later was 2.79.

### **(Effect of the Invention)**

The use of the method of the present invention whereby polymerization is performed in a heating medium makes a large contribution to industry because it has a variety of advantages, including the following.

(1) The polymer is swollen by the heating medium, and polymer viscosity decreases, making it unnecessary to use extreme motive force for agitation.

(2) Polymer pyrolysis and side reactions are prevented because polycondensation can be performed at a low temperature, yielding a high-quality polymer with little coloration.

(3) A high vacuum is not necessary, dispensing with the need for complex equipment and large amounts of energy.

(4) Polyester with a high degree of polymerization can be obtained in a simple manner without using conventional solid phase polymerization.

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## Abstract

(57)【要約】

## 【目的】

重合反応における気-液界面での流動不良を発生させず高品質の高重合度ポリエチレンテレフタレートが得られる製造方法を提供する。

## 【構成】

エステル化反応工程のあとの重縮合反応工程を極限粘度( $\eta$ )が 0.4-0.9dl/g のポリエチレンテレフタレートを得る前段重縮合工程と、極限粘度( $\eta$ )が 0.8-1.3dl/g のポリエチレンテレフタレートが得られる後段重縮合工程に分ける。

その後段重縮合工程を、複数の回転軸 12,13, 及びこれに直角に軸方向に間隔を保って取付けられたパドル 21-26、31-36 とこのパドルの先端部に取り付けられた前記間隔にほぼ相当する長さをもつスクレーパ 41-46、51-56 とで構成された搅拌翼を有し、この搅拌翼の回転直径を D、軸方向長さを L としたとき L/D が 2-10、好ましくは 4-8 の搅拌重工機で行う。

(57) [Abstract]

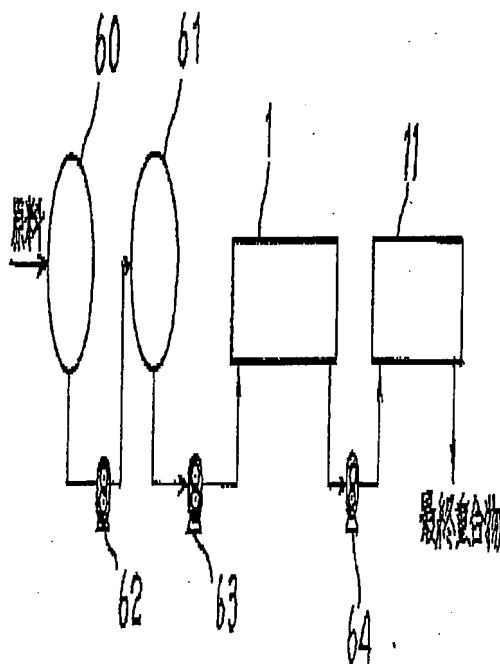
## 【Objective】

Air in polymerization reaction manufacturing method where high degree of polymerization polyethylene terephthalate of high quality where with-liquid interface does not generate defective fluidity is acquired is offered.

## 【Constitution】

condensation polymerization process after esterification reaction process prestage condensation polymerization step. intrinsic viscosity ( $\eta$ ) where intrinsic viscosity ( $\eta$ ) obtains polyethylene terephthalate of 0.4 -0.9 dl/g you divide into poststage condensation polymerization process where polyethylene terephthalate of 0.8 - 1.3 dl/g is acquired.

After that staged polycondensation process, rotating shaft 12,13, of multiple and in this in right angle maintaining spacing at shaft direction, when it possesses impeller blade which with paddle 21-26、31-36 which is installed and scraper 41-46, 51-56 which has length which almost is suitable to aforementioned spacing which is installed in this end of paddle is formed, rotation diameter of this impeller blade designating D、shaft direction length as L L/D 2 - 10, It does with heavy stirring apparatus of preferably 4-8.



## Claims

## 【特許請求の範囲】

## 【請求項 1】

エステル化反応工程と重縮合反応工程により高重合度のポリエチレンテレフタレートを連続的に溶融重縮合して製造する方法において、前記重縮合反応工程が、フェノールと 1,1,2,2-テトラクロロエタンの重量比が 4 対 6 である 20 deg C の混合溶媒中で測定した極限粘度 ( $\eta$ ) が 0.4~0.9dl/g であるポリエチレンテレフタレートを得る前段重縮合工程と、該前段重縮合工程で得られたポリエチレンテレフタレート複数の回転軸と、該回転軸にほぼ直角に軸方向に間隔を保って取付けられた複数のパドル及び該パドルの先端部に前記間隔にほぼ相当する長さをもち前記回転軸に平行に取付けられたスクレーパよりなる攪拌翼とを有し、該攪拌翼はその回転により互いにセルフクリーニングする構造であり、前記攪拌翼の回転直径を D、該攪拌翼の軸方向取付け長さを L で表わした L/D が 2~10、好ましくは 4~8 である少くとも 1 基の攪拌重合機に供給して重縮合反応を行い、前記した極限粘度 ( $\eta$ ) が 0.8~1.3dl/g であるポリエチレンテレフタレートを得る後段重縮合工程とからなることを特徴とする高重合度ポリエチレンテレフタレートの製造方法。

## Specification

## 【発明の詳細な説明】

## 【0001】

## 【産業上の利用分野】

本発明は、高重合度のポリエチレンテレフタレートの製造方法に関し、溶融重合方法で高重合度のポリエチレンテレフタレートを製造する方法に関する。

## 【0002】

## 【従来の技術】

ポリエチレンテレフタレートの連続製造方法においては、最終重合機として従来一軸または二軸攪拌方式の機型反応機が使用されている。

この中でも高重合度のポリマーを得るには、ポリマーの粘度が 10.000 ポイズ以上となることか

## 【Claim(s)】

## 【Claim 1】

melt condensation polymerization doing polyethylene terephthalate of high degree of polymerization in continuous with esterification reaction process, and condensation polymerization process regarding to method which it produces, aforementioned condensation polymerization process, phenol and 1, 1, 2 and 2, -tetrachloroethane weight ratio 4 -to-6 polyethylene terephthalate which is acquired with prestage condensation polymerization step. said prestage condensation polymerization process which obtains polyethylene terephthalate where the intrinsic viscosity ( $\eta$ ) which was measured in mixed solvent of 20 deg C which are is 0.4- 0.9 dl/g rotating shaft of multiple and, In said rotating shaft in almost right angle maintaining spacing at shaft direction, with the structure which possesses impeller blade which consists of scraper which is installed parallel to aforementioned rotating shaft in multiple paddles and the said end of paddle which are installed with length which almost is suitable in aforementioned spacing as for said impeller blade with revolution mutually self-cleaning it does, L/D which displays attached length in shaft direction of D, said impeller blade with L 2 - 10, supplying rotation diameter of aforementioned impeller blade to churning polymerizer of one reactor which is a preferably 4~8 at least, manufacturing method. of high degree of polymerization polyethylene terephthalate where it does condensation polymerization, before consists of poststage condensation polymerization process which obtains polyethylene terephthalate which intrinsic viscosity ( $\eta$ ) which was inscribed is 0.8 - 1.3 dl/g makes feature

## 【Description of the Invention】

## 【0001】

## 【Field of Industrial Application】

It regards method where this invention regards manufacturing method of polyethylene terephthalate of high degree of polymerization, produces polyethylene terephthalate of high degree of polymerization with melt polymerization method.

## 【0002】

## 【Prior Art】

Regarding to continuous production method of polyethylene terephthalate, horizontal reactor of single shaft or dual shaft churning system is used until recently as final polymerizer.

Even among these to obtain polymer of high degree of polymerization, from fact that viscosity of polymer becomes

ら、従来より実願昭 46-62620 号に示されたような二軸式撹拌タイプのものが用いられている。

## [0003]

図 4、図 5 に従来使用されている二軸式重合反応器の断面図を示す。

図 4、図 5 に示す反応器はジャケット 2 を有する反応器 1 の長手方向に平行に 2 本の回転軸 3 が貫通している。

この 2 本の回転軸 3 には、複数の円板状撹拌翼 4 が交互に重なるよう固定されており、回転軸 3 の回転により重合物を撹拌するようになっている。

5 は円板状撹拌翼の外周側に設けられたスクレーパーである。

## [0004]

前記円板状撹拌翼 4 はお互いに逆方向(図 5 参照)に回転するようになっている。

また反応器 1 の上部には揮発物の排気ノズル 6 が設けられており、反応によって副生する揮発物はこの排気ノズル 6 から系外に排気される。

なお、反応器 1 の長手方向の両端近傍には、各々ポリマーの入口 7 及び出口 8 が設けられている。

この反応器 1 内で重合されるべき中間重合物は、ポリマーの入口 7 より反応器 1 内に入り反応器 1 内で重合され出口ノズル 8 より最終重合物として排出される。

## [0005]

反応器 1 内での重合は、反応器 1 内部を数 Torr 以下の真空度とし、温度 270~290 deg C で円板状撹拌翼 4 の回転により重合物を撹拌し、反応副生物等の揮発性ガスを排出ノズル 6 より系外に排出しながら行われる。

## [0006]

## [発明が解決しようとする課題]

前記従来装置において問題となる点は、図 4 に示すように円板状撹拌翼 4 が 2 本の回転軸 3 に交互に取付けられていて、翼側面及び回転軸 3 の外周面の大部分がセルフクリーニングされないため、特に翼側面においては流動が非常に悪化しデッドスペースを生じることである。

10,000 poise or greater, those of kind of two-shaft stirrer type which is shown from until recently in Japan Patent Application Showa 46-62620 number are used.

## [0003]

sectional view of twin shaft type polymerization reactor which is used for Figure 4, Figure 5 until recently is shown.

rotating shaft 3 of 2 has penetrated reactor which is shown in Figure 4, Figure 5 parallel to machine direction of reactor 1 which possesses jacket 2.

In order for disk shaped stirrer blade 4 of multiple to be piled up alternately, we are locked in rotating shaft 3 of this 2, we have reached point where the polymer is agitated due to revolution of rotating shaft 3.

As for 5 it is a scraper which is provided in outer perimeter side of disk shaped stirrer blade.

## [0004]

Aforementioned disk shaped stirrer blade 4 has reached point where it turns mutually to reverse direction (Figure 5 reference).

In addition exhaust nozzle 6 of volatile substance is provided in upper part of the reactor 1, with reaction volatile substance which by-production is done from this exhaust nozzle 6 exhaust is done in outside the system.

Furthermore, inlet 7 and outlet 8 of each polymer are provided in the vicinity of both ends of machine direction of reactor 1.

intermediate polymer which it should polymerize inside this reactor 1 is polymerized inside reactor 1 entering into reactor 1 from inlet 7 of polymer and is discharged as final polymer from outlet nozzle 8.

## [0005]

While polymerization inside reactor 1 designating reactor 1 internal as the degree of vacuum of several Torr or less, agitating polymer with temperature 270~290 deg C due to the revolution of disk shaped stirrer blade 4, from discharge nozzle 6 discharging reaction by-product or other volatile gas in the outside the system it is done.

## [0006]

## [Problems to be Solved by the Invention]

It is as for point which becomes problem description above until recently in equipment, as shown in Figure 4, disk shaped stirrer blade 4 being installed alternately in rotating shaft 3 of 2, because major portion of the outer perimeter surface of blade side surface and rotating shaft 3 self-cleaning it is not done, flow to deteriorate very regarding especially blade side surface and to cause the dead space.

スクレーパー 5 は主として反応器 1 の内壁のポリマーを掻き取るためのものであり、円板状攪拌翼 4 の側面の付着ポリマーは掻き取れない構造となっている。

[0007]

更にもう 1 つの問題点は、図 5 に見られるように円板状攪拌翼 4 の上部において、反応器 1 の内壁との間に空間部を有することにある。

この空間部は、重合物から分離した揮発成分を排気ノズル 6 から排出するために設けられたものであり、反応器 1 内の圧力を均一に保つためのものである。

[0008]

しかし、この場合、重合物と気相部に必ず気-液界面を有することになる。

図 5 の A 部が気-液界面となる。

この部分は反応器 1 の長手方向全域に生じる。

この気-液界面でも流動不良部が生じ、付着ポリマーの更新が極度に悪化し、ジャケット 2 からの伝熱(加熱)が常に行われるため、長時間滞留による重合物の品質劣化が生じ、この劣化した重合物が製品中に混入し製品自体の品質を悪化させる原因となる。

[0009]

本発明は、重合反応における気-液界面での流動不良を回避することにより高品質の高重合度ポリエチレンテレフタレートを製造可能な製造方法を提供することを課題としている。

[0010]

[課題を解決するための手段]

本発明は、エステル化反応工程と重縮合反応工程により高重合度のポリエチレンテレフタレートを連続的に熔融重縮合して製造する方法における前記課題を解決するために、その重縮合反応工程として、フェノールと 1,1,2,2-テトラクロロエタンの重量比が 4 対 6 である 20 deg C の混合溶媒中で測定した極限粘度( $\eta$ )が 0.4~0.9dl/g であるポリエチレンテレフタレートを得る前段重縮合工程と、該前段重縮合工程で得られたポリエチレンテレフタレートを次のように重縮合反応させ、前記した極限粘度( $\eta$ )が 0.8~1.3dl/g であるポリエチレンテレフタレートを得る後段重縮合工

surface and to cause the dead space.

As for scraper 5 with those in order to scrape polymer of inside wall of reactor 1 mainly, as for adhering polymer of side surface of disk shaped stirrer blade 4 it has become structure which cannot be scraped.

[0007]

Furthermore as for problematical point of another, as seen in Figure 5, it is to possess gap between inside wall of reactor 1 in upper part of disk shaped stirrer blade 4.

As for this gap, being something which is provided in order to discharge volatile component which is separated from polymer from exhaust nozzle 6, it is something because it maintains pressure inside reactor 1 at the uniform.

[0008]

But, in this case, be sure to mean to possess air-liquid interface in the polymer and gas phase part.

A part of Figure 5 becomes air-liquid interface.

This portion occurs in machine direction entire area of reactor 1.

defective fluidity section occurs with as many as this air-liquid interface, renewal of adhering polymer deteriorates in polarity, because conducted heat (Heating) from the jacket 2 is always done, degradation of quality of polymer occurs with residence for long periods, this polymer which deteriorates mixing existence does in product and quality of product itself becomes cause which deteriorates.

[0009]

As for this invention, producible manufacturing method is offered designates high degree of polymerization polyethylene terephthalate of high quality as problem air in polymerization reaction by with-liquid interface evading the defective fluidity.

[0010]

[Means to Solve the Problems]

As for this invention, melt condensation polymerization doing polyethylene terephthalate of high degree of polymerization in continuous with esterification reaction process, and condensation polymerization process in order to solve the aforementioned problem in method which it produces, as that condensation polymerization process, phenol and 1, 1, 2 and 2, -tetrachloroethane weight ratio 4 -to-6 following way condensation polymerization doing polyethylene terephthalate which is acquired with prestage condensation polymerization step. said prestage condensation polymerization process which obtains polyethylene terephthalate where intrinsic viscosity ( $\eta_{et}$ ) which was measured in the mixed

程とからなる方法を採用する。

[0011]

すなわち、その後段重縮合工程は、複数の回転軸と、この回転軸にほぼ直角に軸方向に間隔を保って取付けられた複数のパドル及びこのパドルの先端部に前記間隔にほぼ相当する長さをもち回転軸に平行に取付けられたスクレーバよりなる攪拌翼とを有し、該攪拌翼はその回転により互いにセルフクリーニングする構造であり、この攪拌翼の回転直径をD、軸方向取付け長さをLで表わしたL/Dが2~10、好ましくは4~8である少くとも1基の攪拌重合機を用いて重縮合反応を行わせる工程である。

これによって、従来技術の欠点が解消され、極限粘度が0.8~1.3dl/gの品質の良い高分子量の重合物を得ることができる。

[0012]

本発明による高重合度ポリエチレンテレフタレート製造方法の特徴は、重合物の粘度が高くなり、流動性が悪化しやすくなる後段重縮合工程に完全なセルフクリーニング機能を有する前記した構造の重合反応器を用いることにより、反応器内での長期滞留物を無くし、高重合度の品質の良い重合物を得ることができるようにした点である。

[0013]

【作用】

本発明による高重合度ポリエチレンテレフタレート製造方法における操作と作用を添付図面を用いて説明する。

図1は本発明の連続重合方法の一実施態様におけるフローシートを示し、60,61はエステル化反応槽、1は前段重縮合工程を示す重合反応器であり図4、図5に示した従来用いられていた反応器と同様のものである。

11は後段重縮合工程を示す重合反応器であり、図2及び図3にその詳細を示す。

solvent of 20 deg C which are is 0.4 - 0.9 dl/g, Before method which consists of poststage condensationpolymerization process which obtains polyethylene terephthalate where intrinsic viscosity (et)which was inscribed is 0.8 - 1.3 dl/g is adopted.

[0011]

namely, after that as for staged polycondensation process, in rotating shaft and this rotating shaft of multiple in almost right angle maintaining spacing at shaft direction, impeller blade which consists of scraper which is installed parallel to rotating shaft in multiple paddles and this end of paddle which are installed with length which almost is suitable in aforementioned spacing possessing, said impeller blade mutually with structure which self-cleaning is done, is the step which does condensation polymerization rotation diameter of this impeller blade L/D which displays D, attached length in shaft direction with L 2 - 10, making use of churning polymerizer of one reactor which is a preferably 4~8 at least with revolution.

Now, deficiency of Prior Art is cancelled, polymer of high molecular weight where intrinsic viscosity quality of 0.8 - 1.3 dl/g is good can be acquired.

[0012]

As for feature of manufacturing method of high degree of polymerization polyethylene terephthalate, viscosity of polymer becomes high with this invention, loses long period residence ones inside reactor beforepossessing complete self-cleaning function in poststage condensation polymerizationprocess which becomes easy flow property to deteriorate by using polymerization reactor of structure which was inscribed, it is a point which it tries to beable to acquire polymer where quality of high degree of polymerization is good.

[0013]

[Working Principle]

Operation and action in manufacturing method of high degree of polymerization polyethylene terephthalate with this invention areexplained making use of attached figure.

As for Figure 1 it is something which is similar to reactor whereit showed flowsheet in embodiment of continuous polymerization method of this invention, as for60 and 61 as for esterification reaction vessel, 1 with polymerization reactor which shows prestage condensation polymerization process it showed in Figure 4、Figure 5 and isuntil recently used.

11 with polymerization reactor which shows poststage condensation polymerizationprocess, shows details in Figure 2 and Figure 3

62、63、64 は重合物を順次次の反応器へ輸送する輸送手段である。

[0014]

後段重合工程に示した重合反応器の構造及び作用を詳細に図 2 並びに図 3 を用いて説明する。

図 2 及び図 3 に示すように、反応器 11 内には 2 本の回転軸 12,13 が互いに平行に軸支されており、各々の回転軸 12,13 は図示しない駆動源によって、図中矢印のように同一回転方向に同一回転速度で互いに同期して回転駆動されるようになっている。

この反応器 11 の内壁は、回転軸 12,13 をそれぞれ中心とする 2 個の円筒壁 111,112 を繋げたような形の蘭形断面を有している。

回転軸 12,13 はそれぞれ丸軸 121,131 及びその外周部に擬四角断面を持つ軸カバー 122,132 とから構成されている(図 3 参照)。

[0015]

回転軸 12 には、所定の間隔を隔てて複数のパドル 21,22,23,24,25,26 が固定されている。

各パドル 21~26 は、中央部が膨らみ両端が尖った紡錘形断面を持つ厚肉板状に形成されており、各パドル 21~26 は回転軸 12 に対してそれと直交する面内に沿って取付けられ、かつ、回転軸 12 の軸方向に並んで隣接するパドル 21~26 はその軸回りに位相が 90 度ずれた状態となっている。

また、これらのパドル 21~26 の各尖端は、その回転角度位置に応じて僅かなクリアランスを隔てて反応器 11 の円筒壁 111 あるいは後述する対応するパドル 31~36 に対向し得るようにその寸法が選定されている。

[0016]

一方、回転軸 13 にも、同様に、紡錘形断面の複数のパドル 31,32,33,34,35,36 が固定されている。

各パドル 31~36 はそれぞれ前記したパドル 21~26 に対応してそれと同じ軸方向位置に位置し、各々対応するパドル 21~26 に対して各々位相が 90 度ずれた形で回転軸 13 に取付けられている。

また、各パドル 31~36 の各尖端は、その回転角度位置に応じて僅かなクリアランスを隔てて反

2 and Figure 3.

62, 63 and 64 are transport means which transports polymer to sequential following reactor.

[0014]

structure and action of polymerization reactor which is shown in poststage polymerization process in detail are explained making use of Figure 2 and Figure 3.

As shown in Figure 2 and Figure 3, rotating shaft 12,13 of 2 axial support is done mutually parallel to inside reactor 11, each rotating shaft 12,13 with unshown drive source, like the in the diagram arrow synchronization doing mutually with same rotational speed to same rotation direction, is designed in such a way that rotary driving it is done.

As for inside wall of this reactor 11, it has possessed cocoon shaped cross section of kind of shape which can connect cylindrical pipe wall 111,112 of 2 rotating shaft 12,13 is designated as center respectively.

rotating shaft 12,13 is formed from shaft cover 122,132 which has pseudo tetragon cross section in the respective circular axis 121,131 and its perimeter, (Figure 3 reference).

[0015]

multiple paddles 21,22,23,24,25,26 is locked to rotating shaft 12, across predetermined spacing.

Each paddle 21~26 center is formed by thick plate which has spindle-shape cross section where expansion both ends becomes pointed, each paddle 21~26 is installed vis-a-vis rotating shaft 12 that alongside in-plane which crosses, at same time, lining up into shaft direction of rotating shaft 12, as for paddle 21~26 which is adjacent the phase 90 degrees has become state which slips in axial rotation.

In addition, as for each tip of these paddle 21~26, according to rotation angle position in order cylindrical pipe wall 111 of reactor 11 or it mentions later to be possible to oppose to paddle 31~36 which corresponds across slight clearance, dimension is selected.

[0016]

On one hand, in same way, multiple paddles 31,32,33,34,35,36 of spindle-shape cross section is locked to also rotating shaft 13.

As for each paddle 31~36 corresponding to paddle 21~26 which before was inscribed respectively, there is a position of same shaft direction position as that, each phase 90 degrees in form which slips is installed in rotating shaft 13 each vis-a-vis paddle 21~26 which corresponds.

In addition, each tip of each paddle 31~36 cylindrical pipe wall 112 of reactor 11 or each has reached point where it can

応器 11 の円筒壁 112 あるいは各々対応するパドル 21~26 に対向しうようになっている。

[0017]

さらに、パドル 21~26、31~36 の先端部にはそれぞれ、その先端部の断面形状に相当する擬三角形断面のスクレーパ 41~46、51~56 が前記回転軸 12、13 と平行に固定されている。

各スクレーパ 41~46、51~56 の先端面は隣接するパドル 21~26、31~36 に対して軸方向に僅かなクリアランスを隔てて対向している。

[0018]

各スクレーパ 41~46、51~56 は同様な構成であるので、いま代表としてパドル 23 のスクレーパについて詳説すると、パドル 23 両尖端両面には合計 4 個のスクレーパ 43 が取付けられ、両面のスクレーパ 43 の先端はそれぞれパドル 32、34 の側面に近接して対向し得ようになっている。

各スクレーパ 43 の先端縁線はスクレーパ 43 の対応する尖端と同一線上に位置しており、それにより各スクレーパ 43 の先端は回転軸 12 の回転角度位置に応じて僅かなクリアランスを隔てて反応器 11 の円筒壁 111 あるいはパドル 33 と連続する表面を有する軸カバー 132 に対向し得る。

[0019]

また、図 3 に示すように、スクレーパ 43 と軸カバー 122 との間には回転に応じて隣接するパドル 32、34 に取付けられたスクレーパ 52、54 が互いに入り込むようになっており、それらが入り込んだときにスクレーパ 43 の軸中心側の周面とスクレーパ 52、54 の軸中心側の周面とが僅かなクリアランスを隔てて近接するように寸法が選定されている。

以上の構造をもつパドルとスクレーパが本発明という攪拌翼を構成している。

[0020]

このような重合反応器において、重合物は入口 201 から反応器 11 内に入れられ、回転軸 12、13 が駆動回転することでパドル 21~26、31~36 及びスクレーパ 41~46、51~56 の移動による攪拌作用で攪拌され、その後、出口 202 から取出される。

ここで、図 3 の断面図からも判るように回転軸 12、13 とスクレーパ 41~46、51~56 の占める体積が小さく、またパドル 21~26、31~36 も間隔を開けて取付けられているので、反応器 11 内の有

oppose to paddle 21~26 which corresponds across slight clearance according to rotation angle position.

[0017]

Furthermore, respectively, scraper 41~46, 51~56 of pseudotriangular cross section which is suitable to cross section shape of protruding end part is locked parallel with aforementioned rotating shaft 12, 13 in protruding end part of paddle 21~26, 31~36.

Is opposed to shaft direction across slight clearance end face of each scraper 41~46, 51~56 vis-a-vis paddle 21~26, 31~36 which is adjacent.

[0018]

Because each scraper 41~46, 51~56 is similar constitution, now as representation when detailed explanation it does concerning scraper of paddle 23, you can install scraper 43 of total 4 in paddle 23 both tip both surfaces, end of scraper 43 of both surfaces proximity doing in side surface of respective paddle 32, 34, has reached point where it can oppose.

As for end edge line of each scraper 43 there is same linear position as tip to which scraper 43 corresponds and time, with that the end of each scraper 43 cylindrical pipe wall 111 of reactor 11 or paddle 33 can oppose to shaft cover 132 which possesses surface which is continued across slight clearance according to rotation angle position of rotating shaft 12.

[0019]

In addition, way it shows in Figure 3, between scraper 43 and the shaft cover 122 it has reached point where scraper 52, 54 which is installed in paddle 32, 34 which is adjacent according to revolution enters mutually, When those enter, in order surrounding surface of axis center side of scraper 43 and surrounding surface of axis center side of scraper 52, 54 proximity to do across slight clearance, dimension is selected.

impeller blade which paddle and scraper which have structure above say to this invention is formed.

[0020]

In this kind of polymerization reactor, polymer from inlet 201 is inserted into the reactor 11, by fact that rotating shaft 12, 13 drives turns with movement of the paddle 21~26, 31~36 and scraper 41~46, 51~56 is agitated with stirring action, after that, is removed from outlet 202.

As here, understood even from sectional view of Figure 3, volume which rotating shaft 12, 13 and scraper 41~46, 51~56 occupy to be small, in addition paddle 21~26, 31~36 opening spacing, because it is installed, greatly it can increase



有効容積率を従来のセルフクリーニング式の攪拌装置に較べて大幅に増大させることができる。

[0021]

図示例のものでは、有効容積は総容積の70~75%となっている。

なお、必要に応じてパドル 21~26、31~36 の取付間隔を拡げ、その分スクレーパ 41~46、51~56 の長さを長くすることにより、有効容積率を更に増大させることもできる。

一方、上記攪拌作用と同時に下記のクリーニング作用により反応器 11 内各部はセルフクリーニングされる。

[0022]

すなわち、反応器 11 の内壁は、パドル 21~26、31~36 の先端、及びスクレーパ 41~46、51~56 の先端縁線部が近接して移動することによってクリーニングされる。

また、パドル 21~26 とパドル 31~36 の曲面状周面は相互にそれらの先端が近接して移動することによってクリーニングされる。

[0023]

さらに、パドル 21~26、31~36 の平面状側面と、それらに各々対向するスクレーパ 51~56、41~46 の先端面とは、近接して移動することによって互いにクリーニングされる。

例えば、パドル 22 の平面状側面はスクレーパ 51,53 の先端面と近接して相対移動し、それらの対向面が互いにクリーニングされる。

[0024]

また、スクレーパ 41~46、51~56 の周面は互いにスクレーパ 41~46、51~56 同志がその先端及び周面を近接させて移動することで互いにクリーニングされる。

このように、回転軸 12,13 の回転によるパドル 21~26、31~36、スクレーパ 41~46、51~56 の相対移動により容器 11 内の全ての表面を完全にクリーニングすることができる。

[0025]

なお、反応器出口 202 におけるポリマー(最終重合物)の重合度分布をシャープにするためには一般的に、反応器 11 内における処理物の滞留時間分布(=平均滞留時間に対するバラツキ)を均一に近くすることが重要となる。

このためには、攪拌翼の直径(D)に対する軸方向の長さ(L)の比 L/D を大きくするか、あるいは

effective volume ratio inside reactor 11 in comparison with stirring apparatus of conventional self-cleaning type.

[0021]

With those of drawn example, as for effective volume 70 - 75% of total volume it has become.

Furthermore, it expands installation spacing of according to need paddle 21~26、31~36, it is possible also furthermore to increase effective volume ratio that much by making length of scraper 41~46, 51~56 long.

On one hand, simultaneously with above-mentioned stirring action reactor 11 inside section self-cleaning is done by below-mentioned cleaning action.

[0022]

inside wall of namely, reactor 11, tip of paddle 21~26、31~36 and end edge line part of the scraper 41~46, 51~56 doing proximity, cleaning is done it moves by.

In addition, curved surrounding surface of paddle 21~26 and paddle 31~36 those tip doing proximity mutually, cleaning is done it moves by.

[0023]

Furthermore, flat side surface of paddle 21~26、31~36 and each end face of scraper 51~56、41~46 which opposes, proximity doing, cleaning it is done mutually in those it moves by.

end face and proximity of scraper 51,53 doing, relative positioning it does the flat side surface of for example paddle 22, those opposing surface are done cleaning mutually.

[0024]

In addition, surrounding surface of scraper 41~46, 51~56 scraper 41~46, 51~56 proximity doing the end and surrounding surface mutually, cleaning is done mutually by fact that it moves.

This way, cleaning is possible all surface inside container 11 completely with revolution of rotating shaft 12,13 with relative positioning of paddle 21~26、31~36、scraper 41~46, 51~56.

[0025]

Furthermore, in order to designate polymerization degree distribution of polymer (final polymer) in the reactor outlet 202 as sharp, general, residence time distribution (variation for = average residence time) of treated matter inside the reactor 11 is made close in uniform, it becomes important.

For this, it enlarges ratio L/D of length (L) of shaft direction for diameter (D) of impeller blade, or it mounts partition etc,

は、反応器 11 内の軸方向に対して仕切り板等を装着し軸方向の混合を極力抑える必要がある。

【0026】

処理物の粘性によっても異なるが高重合度ポリエチレンテレフタレートを重ね合する場合、粘性も高く(約 1 万~3 万 Poise)、 $L/D=2\sim10$ 、好ましくは 4~8 程度で仕切り板が無くても、良好な滞留時間分布が得られる。

【0027】

なお、上述の例では回転軸を 2 本設けているが、本発明は 2 本に限定されるものではなく、3 本以上設けることも可能である。

また、上述の例ではスクレーパは、凝三角形断面としたが、円柱状、または柱状とすることも可能である。

【0028】

【実施例】

以下、本発明による高重合度ポリエチレンテレフタレート製造方法の実施例について具体的に説明する。

【0029】

(実施例 1)

図 1 に示したフローの装置を使いテレフタル酸 1.0 モル、エチレングリコール 1.5 モルの割合で混合された原料スラリーを毎時 6kg の割合で、連続的に第 1 段目のエステル化槽に供給した。

このスラリー中には触媒としての三酸化アンチモン、安定剤としてのリン酸トリフェニルが原料スラリー中に各々 350ppm、300ppm の割合で添加されている。

エステル化反応は第 1 段、第 2 段のエステル化反応槽で反応率約 96%まで行った。

この時の第 1 段、第 2 段エステル化反応槽の条件は、温度は共に 260 deg C であり、滞留時間は各々 4.5 時間、2 時間であった。

【0030】

次に、このプレポリマーを温度 270 deg C、圧力 2Torr にコントロールされた。

図 5 に示した二軸横型攪拌式前段重合器

vis-a-vis the shaft direction inside reactor 11 and it is necessary mixture of shaft direction the to the utmost to hold down.

【0026】

It differs even in viscosity of treated matter, but when high degree of polymerization polyethylene terephthalate is polymerized, also viscosity is high (Approximately 10,000 - 30,000 Poise), there not being a partition with  $L/D=2\sim10$ , preferably 4~8 extent, satisfactory residence time distribution is acquired.

【0027】

Furthermore, with above-mentioned example rotating shaft is provided 2, but this invention is not something which is limited in 2, 3 or more also it is possible to provide.

In addition, with above-mentioned example as for scraper, it made pseudotriangular cross section, but also it is possible to make cylinder, or prism.

【0028】

【Working Example(s)】

Below, you explain concretely with this invention concerning Working Example of high degree of polymerization polyethylene terephthalate production method.

【0029】

(Working Example 1)

equipment of flow which is shown in Figure 1 was used and the starting material slurry which is mixed at ratio of terephthalic acid 1.0 mole, ethyleneglycol 1.5 mole at ratio of each hour 6 kg, was supplied to esterification tank of first step in continuous.

triphenyl phosphate as antimony trioxide, stabilizer as catalyst in this slurry is added in the starting material slurry at ratio of each 350 ppm, 300 ppm.

With esterification reaction vessel of first step, second step it did esterification reaction up to reaction ratio approximately 96%.

As for condition of first step, second step esterification reaction vessel of this time, as for temperature with 260 deg C, as for residence time they were each 4.5 hours, 2 hours together.

【0030】

Next, this prepolymer was controlled to temperature 270 deg C, pressure 2 Torr.

In twin screw horizontal type stirred type front stage

(L/D=4, 攪拌翼回転直径 166mm, 内容積 18 リットル, 攪拌回転数 20rpm) に、第 2 段エステル化槽出口のギヤポンプで押込み、滞留時間約 2 時間で重合させた。

得られたポリマーの極限粘度( $\eta$ )は、0.64dl/g であった。

[0031]

次にこのポリマーを、温度 275 deg C, 圧力 0.3Torr にコントロールされた図 2 に示したセルフクリーニング機能を有する二軸横型攪拌式後段重合器(L/D=6, 攪拌翼回転直径 100mm, 内容積 6 リットル, 攪拌回転数 30rpm) に、前記前段重合器出口のギヤポンプ 64 で押込み、滞留時間 40 分で重合させた。

得られたポリマーの極限粘度( $\eta$ )は、1.12dl/g であった。

他の試験結果を表 1 に示す。

[0032]

(実施例 2)

実施例 1 における後段重合器において、圧力を 0.1Torr とした以外は実施例 1 と同様な重合を行って、得られたポリマーについて同様な分析を行った。

結果を表 1 に示す。

[0033]

(実施例 3)

実施例 1 において、後段重合器の圧力を 1.0Torr とした以外は実施例 1 と同様な重合を行って得られたポリマーについて同様な分析を行った。

結果を表 1 に示す。

[0034]

(実施例 4)

実施例 1 において、前段重合器出口のギヤポンプ 64 から後段重合器に送るポリマーを 1 部連続的に系外に抽出し、後段重合器へ送るポリマーを少なくし、後段重合器の滞留時間を 60 分とした以外は実施例 1 と同様な重合を行って得られたポリマーについて同様な分析を行った。

polymerizer (L/D=4, impeller blade rotation diameter 166 mm, internal volume 18 liter, stirring speed 20 rpm) which is shown in Figure 5, with gear pump of the second step esterification tank outlet you polymerized with pushing in and residence time approximately 2 hours.

intrinsic viscosity ( $\eta$ ) of polymer which it acquires was 0.64 dl/g.

[0031]

Next this polymer, in twin screw horizontal type stirred type poststage polymerization vessel (L/D=6, impeller blade rotation diameter 100 mm, internal volume 6 liter, stirring speed 30 rpm) which possesses self-cleaning function which is shown in Figure 2 which is controlled to temperature 275 deg C, pressure 0.3 Torr, with the gear pump 64 of aforementioned front stage polymerizer outlet was polymerized with pushing in and residence time 40 min.

intrinsic viscosity ( $\eta$ ) of polymer which it acquires was 1.12 dl/g.

Other test result is shown in Table 1.

[0032]

(Working Example 2)

Other than designating pressure as 0.1 Torr in poststage polymerization vessel in the Working Example 1, doing polymerization which is similar to Working Example 1, you analyzed in same way concerning polymer which it acquires.

Result is shown in Table 1.

[0033]

(Working Example 3)

In Working Example 1, other than designating pressure of poststage polymerization vessel as 1.0 Torr, doing polymerization which is similar to Working Example 1, you analyzed in same way concerning polymer which it acquires.

Result is shown in Table 1.

[0034]

(Working Example 4)

In Working Example 1, polymer which is sent to poststage polymerization vessel from gear pump 64 of front stage polymerizer outlet it decreased polymer which in 1 part continuous is sent to the extract and poststage polymerization vessel in outside the system, other than designating residence time of poststage polymerization vessel as 60 min, doing polymerization which is similar to Working Example 1, it

結果を表 1 に示す。

【0035】

(比較例)

実施例 1 の後段重合器形式を前段重合器と同一のものとし、(但し、内容積は 10 リットルのものを用いた)、滞留時間 60 分とした以外は実施例 1 と同様な重合を行って、得られたポリマーについて同様な分析を行った。

結果を表 1 に示す。

【0036】

【表 1】

	極限粘度 ( $\eta$ ) dl/g	外 観 (目視による)	末端カルボキシ基濃度 meq/kg
実施例 1	1.12	異常なし	26
実施例 2	1.28	異常なし	29
実施例 3	0.92	異常なし	25
実施例 4	1.24	異常なし	32
比較例	0.89	ポリマーが黄色に着色	41

上記極限粘度と末端カルボキシ基濃度の分析方法は次のとおりである。

- (1) 極限粘度 ( $\eta$ ) フェノールと 1, 1, 2, 2-テトラクロロエタンの重量比が 4 対 6 である 20℃ の混合溶媒を用いてウペローデ粘度計を用いて測定した。
- (2) 末端カルボキシ基濃度 ポリマー試料を、オルトクレゾールに加熱下、溶解し、クロロホルムを加えながら冷却したサンプルを水酸化カリウム (KOH) にて、滴定し、サンプルの PH 値が 8.8 となる滴定量より算出した。

【0037】

analyzed in same way concerning polymer which itacquires.

Result is shown in Table 1.

【0035】

(Comparative Example)

It designated poststage polymerization vessel form of Working Example 1 as same ones, as front stage polymerizer (However, internal volume used those of 10 liter.), other than making residence time 60 min, doing polymerization which is similar to Working Example 1, it analyzed in same way concerning polymer which it acquires.

Result is shown in Table 1.

【0036】

【Table 1】

## 【発明の効果】

本発明によれば、テレフタル酸とエチレングリコールの混合物を、エステル化反応させるエステル化工程のあと、このエステル化工程で得られたプレポリマーを重縮合反応させて、極限粘度( $\eta$ )が 0.4~0.9dl/g であるポリエチレンテレフタレートを得る前段重縮合工程、及びこの前段重縮合工程で得られたポリエチレンテレフタレートを更に高重合度化するためにセルフクリーニング機構を有する特定の二軸横型攪拌式重合器にて重縮合反応を行い、極限粘度( $\eta$ )が 0.8~1.3dl/g であるポリエチレンテレフタレートを得る後段重縮合工程を経てポリエチレンテレフタレートを製造するので、高重合度で品質の優れたポリエチレンテレフタレートが得られる。

## 【図面の簡単な説明】

## 【図1】

本発明の一実施態様におけるポリエチレンテレフタレート製造のフローを示す工程図。

## 【図2】

図1中の後段重縮合反応器の断面図。

## 【図3】

図2中の 11-11 線に沿う断面図。

## 【図4】

従来より使用されている二軸式重合反応器の断面図。

## 【図5】

図4中の I-I 線に沿う断面図。

## 【符号の説明】

1

前段重合反応器

11

後段重合反応器

111

円筒壁

112

円筒壁

## 【Effects of the Invention】

According to this invention, after esterification step which blend of terephthalic acid and ethyleneglycol, esterification reaction is done, condensation polymerization doing obtained prepolymer with this esterification step, the prestage condensation polymerization step, which obtains polyethylene terephthalate where intrinsic viscosity ( $\eta_{\text{et}}$ ) is 0.4 - 0.9 dl/g and with specific twin screw horizontal type stirred type polymerization vessel which possesses self-cleaning mechanism in order is acquired polyethylene terephthalate which furthermore degree of polymerization raising to do with this prestage condensation polymerization process condensation polymerization action, Passing by poststage condensation polymerization process which obtains polyethylene terephthalate where intrinsic viscosity ( $\eta_{\text{et}}$ ) is 0.8 - 1.3 dl/g because it produces polyethylene terephthalate, polyethylene terephthalate where quality is superior in high degree of polymerization is acquired.

## 【Brief Explanation of the Drawing(s)】

## 【Figure 1】

process diagram, which shows flow of polyethylene terephthalate production in embodiment of the this invention

## 【Figure 2】

sectional view, of poststage polycondensation reactor in Figure 1

## 【Figure 3】

sectional view, which parallels to 11 - 11 lines in Figure 2

## 【Figure 4】

sectional view, of twin shaft type polymerization reactor which is used from until recently

## 【Figure 5】

sectional view, which parallels to I-I line in Figure 4

## 【Explanation of Symbols in Drawings】

1

prepolymerization reactor

11

poststage polymerization reactor

111

cylindrical pipe wall

112

cylindrical pipe wall

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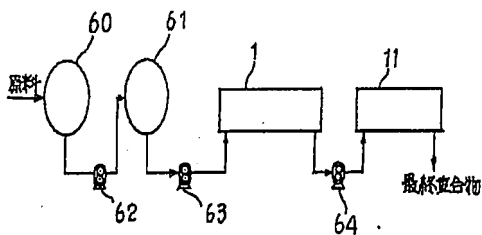
1996-1-9

12	12
回転軸	rotating shaft
122	122
軸カバー	shaft cover
13	13
回転軸	rotating shaft
132	132
軸カバー	shaft cover
21	21
パドル	paddle
22	22
パドル	paddle
23	23
パドル	paddle
24	24
パドル	paddle
25	25
パドル	paddle
26	26
パドル	paddle
31	31
パドル	paddle
32	32
パドル	paddle
33	33
パドル	paddle
34	34
パドル	paddle
35	35
パドル	paddle
36	36
パドル	paddle
41	41
スクレーパ	scraper
42	42

スクレーパ	scraper
43	43
スクレーパ	scraper
44	44
スクレーパ	scraper
45	45
スクレーパ	scraper
46	46
スクレーパ	scraper
51	51
スクレーパ	scraper
52	52
スクレーパ	scraper
53	53
スクレーパ	scraper
54	54
スクレーパ	scraper
55	55
スクレーパ	scraper
56	56
スクレーパ	scraper
60	60
エステル化反応槽	esterification reaction vessel
61	61
エステル化反応槽	esterification reaction vessel

## Drawings

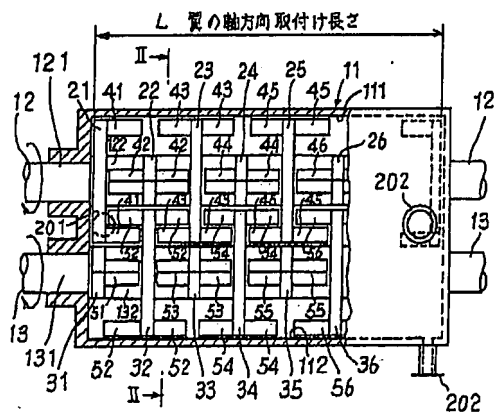
【図1】



【図2】

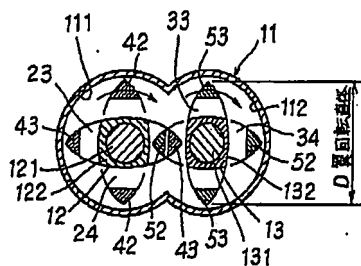
[Figure 1]

[Figure 2]



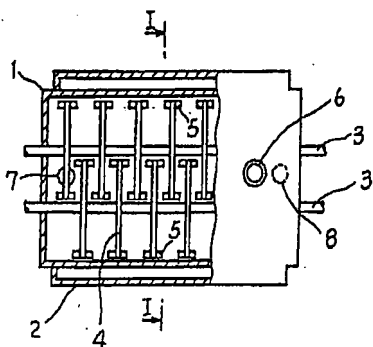
【図3】

[Figure 3]



【図4】

[Figure 4]



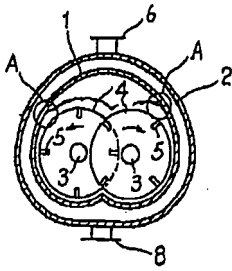
【図5】

[Figure 5]



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熱安定で、アンチモンを含まない無彩色のポリエステル類およびこの方法によって製造することのできる製造物

(54) [Title of Invention]

WITH THERMALLY STABLE, PRODUCT WHICH CAN DO POLYESTERS OF COLORLESS WHICH DOES NOT INCLUDE ANTIMONY AND TO PRODUCE WITH THIS METHOD

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## Abstract

(57) [要約]

(修正有)

[課題]

熱安定で、アンチモンを含まない無彩色のポリエステルを製造するための方法、および、この方法によって製造される製造物を提供する。

[解決手段]

エステル交換が、エステル交換触媒 20~120ppm の存在中で行われ、ついで、エステル化またはエステル交換が終了した後、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体が、エステル化もしくはエステル交換バッチに、錯形成剤として、使用されるエステル交換触媒に対する当量の 100%量および使用されるコバルトに対する当量の 99%以下の量加えられ、コバルト化合物の形態のコバルト 80ppm 以下が、バッチに加えられ、重縮合が、アンチモンを加えることなく、チタン化合物の形態で加えられるチタン 1~10ppm の存在中、適当とあらば、架橋構造基を与える有機化合物 1,000ppm 以下、および、適当とあらば、蛍光増白剤 50ppm 以下の存在で行われる方法。

## Claims

[特許請求の範囲]

[請求項 1]

芳香族ジカルボン酸の脂肪族ジオールによるエステル化または芳香族ジカルボン酸低級脂肪族エステルの脂肪族ジオールによるエステル交換、および、続く重縮合による、熱安定で、アンチモンを含まない無彩色のポリエステルを製造するための方法であって、該方法が、

可能なエステル交換が、触媒金属基準で、エステル交換触媒 20~120ppm の存在中で行われ、

ついで、エステル化またはエステル交換が終了した後、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体が、エステル化もしくはエステル交換バッチに、錯形成剤として、使

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Yuasa Kyojo (6 others)

(57) [Abstract]

(There is an amendment.)

[Problems to be Solved by the Invention]

With thermally stable, method in order to produce polyester of colorless which does not include antimony. And, product which is produced with this method is offered.

[Means to Solve the Problems]

After ester exchange, is done while existing of ester exchange catalyst 20~120 ppm, next, esterification or transesterification ends, phosphoric acid, phosphorous acid and/or phosphonic acid or in esterification or ester exchange batch, quantitative adding of 99% or less of equivalent for 100% quantity of equivalent for ester exchange catalyst which is used as complexing agent, and cobalt which is used those derivative, cobalt 80 ppm or less of morphological form of cobalt compound, in addition to batch, the condensation polymerization, while existing of titanium 1~10 ppm which is added with morphological form of titanium compound without adding antimony, suitableness and an organic compound 1,000 ppm or less, and suitableness which give mule and crosslinked structure basis a method. which is done in existence of mule and fluorescent whitener 50 ppm or less

[Claim(s)]

[Claim 1]

With aliphatic diol of aromatic dicarboxylic acid with aliphatic diol of esterification or aromatic dicarboxylic acid lower fatty ester ester exchange, and, with condensation polymerization which continues, with thermally stable, with method in order to produce polyester of colorless which does not include antimony, said method,

Possible ester exchange, with catalyst metal standard, while existing of ester exchange catalyst 20~120 ppm action,

After next, esterification or transesterification ends, phosphoric acid, phosphorous acid and/or phosphonic acid or in esterification or ester exchange batch, in batch adding cobalt 80 ppm or less of morphological form of quantitative

用されるエステル交換触媒に対する当量の 100%量および使用されるコバルトに対する当量の 99%以下の量加えられ、コバルト化合物の形態のコバルト 80ppm 以下が、バッチに加えられ、

重縮合が、アンチモンを加えることなく、チタン化合物の形態で加えられるチタン 1~10ppm の存在中、適当とあらば、架橋構造基を与える有機化合物(ペタエリスリトール)1,000ppm 以下、および、適当とあらば、蛍光増白剤 50ppm 以下の存在で行われる方法。

#### 【請求項 2】

エステル化またはエステル交換が終了した後、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体が、エステル化もしくはエステル交換バッチに、錯形成剤として、使用されるエステル交換触媒に対する当量の 100%量および使用されるコバルトに対する当量の 90~99%量加えられる、請求項 1 に記載の方法。

#### 【請求項 3】

重縮合が、アンチモンを加えることなく、ジクロロ酢酸中 25 deg C で測定した固有粘度 (IV) 0.4~0.9dl/g 以下で、溶融物中でのカルボキシル濃度 10~50mm/kg 以下で、ついで、固相で所望される最終粘度以下であるチタン 1~10ppm の存在で行われる、請求項 1 および 2 の少なくとも 1 項に記載の方法。

#### 【請求項 4】

コバルト化合物の形態のコバルト 20~40ppm 以下が、バッチに加えられる、請求項 1~3 の少なくとも 1 項に記載の方法。

#### 【請求項 5】

重縮合が、アンチモンを加えることなく、チタン 2~8ppm の存在中、適当とあらば、架橋構造基を与える有機化合物 1,000ppm 以下の存在で行われる、請求項 1~4 の少なくとも 1 項に記載の方法。

#### 【請求項 6】

重縮合が、架橋構造基を与える有機化合物 100~500ppm の存在で行われる、請求項 1~5 の少なくとも 1 項に記載の方法。

#### 【請求項 7】

重縮合が、アンチモンを加えることなく、蛍光増白剤 25ppm 以下の存在で行われる、請求項 1~6 の少なくとも 1 項に記載の方法。

adding those derivative, cobalt compound of 99% or less of equivalent for 100% quantity of equivalent for ester exchange catalyst which is used as complexing agent, and cobalt which is used,

condensation polymerization, while existing of titanium 1~10 ppm which is added with morphological form of titanium compound without adding antimony, suitableness and an organic compound which gives mule and crosslinked structure basis (ペタ erythritol) 1,000 ppm or less, and, suitableness a method. which is done in existence of mule and fluorescent whitener 50 ppm or less

#### 【Claim 2】

After esterification or transesterification ends, phosphoric acid, phosphorous acid and/or phosphonic acid or 90 - 99% quantity of equivalent for 100% quantity of equivalent for ester exchange catalyst which is used as complexing agent, and cobalt which is used it can add to esterification or ester exchange batch, those derivative, method. which is stated in Claim 1

#### 【Claim 3】

condensation polymerization, inherent viscosity which was measured with 25 deg C in dichloroacetic acid without adding antimony, (IV) with 0.4 - 0.9 dl/g or less, with carboxyl concentration 10~50 mm/kg or less in melt, is done in existence of titanium 1~10 ppm which is below final viscosity which next, is desired with solid phase, method. which Claims 1 and 2 states at least in one claim

#### 【Claim 4】

It can add to batch cobalt 20~40 ppm or less of morphological form of cobalt compound, method. which Claim 1~3 states at least in one claim

#### 【Claim 5】

condensation polymerization, while existing of titanium 2~8 ppm, suitableness a is done in existence of organic compound 1,000 ppm or less which gives mule and crosslinked structure basis without adding antimony, method. which Claim 1~4 states at least in the one claim

#### 【Claim 6】

condensation polymerization, is done in existence of organic compound 100~500 ppm which gives crosslinked structure basis, method. which Claim 1~5 states at least in one claim

#### 【Claim 7】

condensation polymerization, is done in existence of fluorescent whitener 25 ppm or less without adding antimony, method. which Claim 1~6 states at least in one claim

## 【請求項 8】

芳香族ジカルボン酸もしくはヒドロキシカルボン酸の脂肪族ジオールによるエステル化または芳香族ジカルボン酸もしくはヒドロキシカルボン酸の低級脂肪族エステルの脂肪族ジオールによるエステル交換、および、繰く重縮合による、請求項 1~7 の少なくとも 1 項に記載の方法であって、

式 III:

HOOC-X-COOH (III)

で表される芳香族ジカルボン酸またはその低級脂肪族エステル 80~100mol%、および、式 IV:

HO-X<sup>1</sup>-COOH (IV)

で表される芳香族ヒドロキシカルボン酸またはその低級脂肪族エステル 0~20mol%を、式 V:

HO-Y-OH (V)

で表されるジオールで、エステル化またはエステル交換する方法であり、

上記式中、X は、ジカルボン酸およびヒドロキシカルボン酸の合計量基準で、5~16 個、好ましくは、6~12 個の炭素原子を有する芳香族基を 80mol%以上、および、4~10 個、好ましくは、6~8 個の炭素原子を有する脂肪族基 20mol%以下であり、X<sup>1</sup> は、p-フェニレン基であり、Y は、エステル交換またはエステル化されたジオールの合計量基準で、2~4 個の炭素原子を有するアルキレンもしくはポリメチレンまたは 6~10 個の炭素原子を有するシクロアルカンもしくはジメチレンシクロアルカン基少なくとも 80mol%、および、4~16 個、好ましくは、4~8 個の炭素原子を有する直鎖もしくは分岐アルカンジイルまたは式  $-(C_2H_4-O)_n-C_2H_4-$  (式中、n は、1~40 の整数である) で表される基 20mol%以下であり、n は、好ましくは、20mol%以下の含量に対して、1 または 2 であり、n=10~40 の基が、好ましくは、5mol%未満の含量しか存在しない方法。

## 【請求項 9】

X が、ジカルボン酸およびヒドロキシカルボン酸の合計量基準で、p-フェニレン基 90~100mol%、m-フェニレン基 0~7mol%、および、4~10 個、好ましくは、6~8 個の炭素原子を有する脂肪族基 0~5mol%であり、X<sup>1</sup> が、p-フェニレン基であり、Y が、エステル交換またはエステル化されたジオールの合計量基準で、2~4 個の炭素原子を有するアルキレンもしくはポリメチレンまたは 6~10 個の炭素原子を有するシクロアルカンもしくはジメ

claim

## 【Claim 8】

With aliphatic diol of aromatic dicarboxylic acid or hydroxy carboxylic acid with the aliphatic diol of lower fatty ester of esterification or aromatic dicarboxylic acid or hydroxy carboxylic acid ester exchange, and, with condensation polymerization which continues, with method which Claim 1~7 states at least in one claim,

Formula III:

HOOC-X-COOH (III)

So aromatic dicarboxylic acid which is displayed or lower fatty ester 80~100 mol%, and Formula IV:

HO-X<sup>1</sup>-COOH (IV)

So aromatic hydroxycarboxylic acid which is displayed or lower fatty ester 0~20 mol%, Formula V:

HO-Y-OH (V)

So with diol which is displayed, esterification or transesterification with method which is done,

In above Formula, as for X, with total amount standard of dicarboxylic acid and the hydroxycarboxylic acid, 5 - 16, aromatic group which possesses carbon atom of preferably, 6~12 80 mol % or more, and, 4 - 10, preferably, 6~8 with aliphatic group 20 mol % or less where has carbon atom; as for X<sup>1</sup>, with p-phenylene group; As for Y, with total amount standard of diol which transesterification or esterification is done, alkylene or polymethylene which possess carbon atom of 2 - 4 or cycloalkane or dimethylene cycloalkane group which possess 6 - 10 carbon atom at least 80 mol%, and, 4 - 16, straight or branched alkane diyl or formula where preferably, 4~8 has carbon atom -  $(C_2H_4-O)$  - with group 20 mol % or less which is displayed with (In Formula, n is integer 1 - 40.), as for n, Vis-a-vis content of preferably, 20 mol % or less, with 1 or 2, basis of n=10~40, only content under preferably, 5 mol% method, which does not exist

## 【Claim 9】

X, with total amount standard of dicarboxylic acid and hydroxycarboxylic acid, p-phenylene group 90~100 mol%, m-phenylene group 0~7 mol%, and 4 - 10, preferably, 6~8 with aliphatic group 0~5 mol% where has carbon atom; X<sup>1</sup>, with p-phenylene group; Y, with total amount standard of diol which transesterification or esterification is done, the alkylene or polymethylene which possess carbon atom of 2 - 4 or cycloalkane or dimethylene cycloalkane group which possess 6 - 10 carbon atom at least 90 mol%, and, 4 -

チレンシクロアルカン基少なくとも 90mol%、および、4~16 個、好ましくは、4~8 個の炭素原子を有する直鎖もしくは分岐アルカンジールまたは式  $-(C_2H_4-O)_n-C_2H_4-$  (式中、n は、1 または 2 の数である) で表される基 10mol% 以下である、請求項 1~8 の少なくとも 1 項に記載の方法。

## 【請求項 10】

芳香族ジカルボン酸および脂肪族ジオールを基体とした熱安定で、アンチモンを含まない無彩色のポリエステルであり、請求項 1 に記載の方法によって製造することができ、艶消しなしの状態、その色数成分が、

a *	-3~+3の範囲、					
a *	- 3 - Range + 3,					
b *	-6~+6の範囲、		および、			
b *	- 6 - Range + 6,		And,			
L *	55	75の範囲で	あるポリ	ス	テ	ル。
L *	55	With range of 75	A certain poly	ス	テ	jp11。

## 【請求項 11】

請求項 10 に記載した芳香族ジカルボン酸および脂肪族ジオールを基体とした熱安定であり、アンチモンを含まない無彩色のポリエステルであり、アンチモンを含まず、チタン 1~10ppm、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体との触媒的に不活性な錯体形態のエステル交換触媒金属 20~120ppm、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体との触媒的に不活性な錯体形態で一部存在するコバルト 0~80ppm、および、場合によっては蛍光増白剤 50ppm 以下を含むポリエステル。

## 【請求項 12】

請求項 10 および 11 の少なくとも 1 項に記載の熱安定で、アンチモンを含まない無彩色のポリエステルであり、

アンチモンを含まず、

チタン 2~8ppm、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体との触媒的に不活性な錯体形態の(金属として計算した)マンガ 50~90ppm、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体との触媒的に不活性な錯体形態で一部存在するコバル

16, straight or branched alkane diyl or formula where preferably, 4~8 has carbon atom -  $(C_2H_4-O)_{<sub>n</sub>-C_2H_4-$  is group 10 mol % or less which is displayed with (In Formula, n is quantity of 1 or 2.), method. which Claim 1~8 states at least in one claim

## 【Claim 10】

With thermally stable which designates aromatic dicarboxylic acid and aliphatic diol as substrate, with polyester of colorless which does not include antimony, produces with method which is stated in Claim 1 to be possible, with state of antitarnish none, color number component,

## 【Claim 11】

cobalt 0~80 ppm, which with thermally stable which designates aromatic dicarboxylic acid and the aliphatic diol which are stated in Claim 10 as substrate, with polyester of colorless which does not include antimony, does not include the antimony, titanium 1~10 ppm, phosphoric acid, phosphorous acid and/or phosphonic acid or in catalytic of those derivative in catalytic ester exchange catalyst metal 20~120 ppm, phosphoric acid, phosphorous acid and/or phosphonic acid of inert complex morphological form or those derivative with inert complex morphological form part exists and, When depending, polyester, which includes fluorescent whitener 50 ppm or less

## 【Claim 12】

With thermally stable which Claim 10 and 11 state at least in one claim, with polyester of colorless which does not include antimony,

antimony implication,

titanium 2~8 ppm, phosphoric acid, phosphorous acid and/or phosphonic acid or of those derivative in catalytic in catalytic of (It calculated as metal.) manganese 50~90 ppm, phosphoric acid, phosphorous acid and/or phosphonic acid or those derivative of inert complex morphological form with inert complex morphological form part cobalt 20~40 ppm,

ト 20~40ppm、および、場合によっては蛍光増白剤 25ppm 以下を含むポリエステル。

【請求項 13】

請求項 10~12 の少なくとも 1 項に記載の熱安定で、アンチモンを含まない無彩色のポリエステルであり、艶消しなしの状態、その色数成分が、 $a^* -2 \sim +2$  の範囲、

and when it exists depending, polyester, which includes fluorescent whitener 25 ppm or less

【Claim 13】

With thermally stable which Claim 10~12 states at least in one claim, with the polyester of colorless which does not include antimony, with state of antitarnish none, color number component, range of  $a^* -2 \sim +2$ ,

b *	-3.5 ~ +3.5 の範囲、および、
b *	-3.5 - +3.5 ranges, and,
L *	60 ~ 70 の範囲であるポリエステル。
L *	polyester, which is a range 60 - 70

【請求項 14】

請求項 10~13 の少なくとも 1 項に記載の熱安定で、アンチモンを含まない無彩色のポリエステルであり、コバルトの 90~99%が、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体との一以上の触媒的に不活性な錯体形態であるポリエステル。

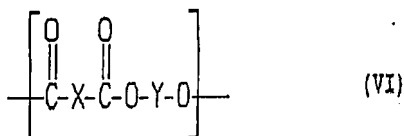
【請求項 15】

請求項 10~14 の少なくとも 1 項に記載の熱安定で、アンチモンを含まない無彩色のポリエステルであり、蛍光増白剤 5~25ppm を含むポリエステル。

【請求項 16】

請求項 10~15 の少なくとも 1 項に記載の熱安定で、アンチモンを含まない無彩色のポリエステルであって、そのポリマー鎖が、

式 VI:



【化 1】

で表される構造基 80~100mol%と、式 VII:

【化 2】

【Claim 14】

With thermally stable which Claim 10~13 states at least in one claim, with the polyester of colorless which does not include antimony, 90 - 99% of the cobalt, phosphoric acid, phosphorous acid and/or phosphonic acid or polyester, which is a inert complex morphological form in catalytic of one or more of those derivative

【Claim 15】

With thermally stable which Claim 10~14 states at least in one claim, with the polyester of colorless which does not include antimony, polyester, which includes fluorescent whitener 5~25 ppm

【Claim 16】

With thermally stable which Claim 10~15 states at least in one claim, with the polyester of colorless which does not include antimony, polymer chain,

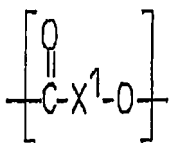
Formula VI:

【Chemical Formula 1】

So structural group 80~100 mol% and Formula VII: which are displayed

【Chemical Formula 2】





(VII)

で表される構造基 20~0mol%とから形成され、

上記式中、X が、5~16 個、好ましくは、6~12 個の炭素原子を有する芳香族基 80mol%以上、および、4~10 個の炭素原子、好ましくは、6~8 個の炭素原子を有する脂肪族基 20mol%以下であり、X<sup>1</sup> が、p-フェニレン基であり、Y が、2~4 個の炭素原子を有するアルキレンもしくはポリメチレンまたは 6~10 個の炭素原子を有するシクロアルカンもしくはジメチレンシクロアルカン基少なくとも 80mol%、および、4~16 個、好ましくは、4~8 個の炭素原子を有する直鎖もしくは分岐アルカンジールまたは式-(C<sub>2</sub>H<sub>4</sub>-O)<sub>n</sub>-C<sub>2</sub>H<sub>4</sub>-(式中、n は、1~40 の整数である)で表される基 20mol%以下であり、n は、好ましくは、20mol%以下の含量に対して、1 または 2 であり、n=10~40 の基が、好ましくは、5mol%未満の含量しか存在しないポリエステル。

## 【請求項 17】

請求項 10~16 の少なくとも 1 項に記載の熱安定で、アンチモンを含まない無彩色のポリエステルであって、

X が、p-フェニレン基 90~100mol%、m-フェニレン基 0~7mol%、および、4~10 個、好ましくは、6~8 個の炭素原子を有する脂肪族基 0~5mol%であり、Y が、2~4 個の炭素原子を有するアルキレンもしくはポリメチレンまたは 6~10 個の炭素原子を有するシクロアルカンもしくはジメチレンシクロアルカン基少なくとも 90mol%、4~16 個、好ましくは、4~8 個の炭素原子を有する直鎖もしくは分岐アルカンジールまたは式-(C<sub>2</sub>H<sub>4</sub>-O)<sub>n</sub>-C<sub>2</sub>H<sub>4</sub>-(式中、n は、1 または 2 の数である)で表される基 10mol%以下である、式 IV で表される構造基からなるポリエステル。

## 【請求項 18】

請求項 10~17 の少なくとも 1 項に記載の熱安定で、アンチモンを含まない無彩色のポリエステルであって、

X が、p-フェニレン基 93~99mol%および m-フェニレン基 1~7mol%である、式 IV で表される構造基によって構成されるポリエステル。

## 【請求項 19】

So it is formed from structural group 20~0 mol% which is displayed,

In above Formula, X, 5 - 16, aromatic group 80 mol % or more, and 4 - 10 carbon atom, preferably, 6~8 which possess carbon atom of preferably, 6~12 with aliphatic group 20 mol % or less where has carbon atom; X<sup>1</sup>, with p-phenylene group; Y, alkylene or polymethylene which possess carbon atom of 2 - 4 or cycloalkane or dimethylene cycloalkane group which possess 6 - 10 carbon atom at least 80 mol%, and, 4 - 16, straight or branched alkane di yl or formula where preferably, 4~8 has carbon atom -(C<sub>2</sub>H<sub>4</sub>-O) <sub>n</sub>-C<sub>2</sub>H<sub>4</sub>- with group 20 mol % or less which is displayed with (In Formula, n is integer 1 - 40. ), as for the n, vis-a-vis content of preferably, 20 mol % or less, with 1 or 2, Basis of n=10~40, only content under preferably, 5 mol% polyester, which does not exist

## 【Claim 17】

With thermally stable which Claim 10~16 states at least in one claim, with the polyester of colorless which does not include antimony,

X, p-phenylene group 90~100 mol%, m-phenylene group 0~7 mol%, and 4 - 10, preferably, 6~8 with aliphatic group 0~5 mol% where has carbon atom; Y, alkylene or polymethylene which possess carbon atom of 2 - 4 or cycloalkane or dimethylene cycloalkane group which possess 6 - 10 carbon atom at least straight or branched alkane di yl or formula where 90 mol%, 4~16, preferably, 4~8 has carbon atom -(C<sub>2</sub>H<sub>4</sub>-O) <sub>n</sub>-C<sub>2</sub>H<sub>4</sub>- is group 10 mol % or less which is displayed with (In Formula, n is quantity of 1 or 2. ), polyester. which consists of structural group which is displayed with Formula IV

## 【Claim 18】

With thermally stable which Claim 10~17 states at least in one claim, with the polyester of colorless which does not include antimony,

X, is p-phenylene group 93~99 mol% and m-phenylene group 1~7 mol%, polyester. which is formed with structural group which is displayed with Formula IV

## 【Claim 19】

請求項 10~18 の少なくとも 1 項に記載の熱安定で、アンチモンを含まない無彩色のポリエステルであって、触媒的に不活性なマンガン錯体およびコバルト錯体が、亜リン酸またはそのエステルとの錯体であるポリエステル。

【請求項 20】

請求項 10~19 の少なくとも 1 項に記載の熱安定で、アンチモンを含まない無彩色のポリエステルであって、場合によっては架橋構造基 1,000ppm 以下を含むポリエステル。

Specification

【発明の詳細な説明】

【0001】

【発明の属する技術分野】

本発明は、再現が極めて容易であり、チタン重縮合触媒を極めて少量添加する場合にも極めて速い重合速度を有し、熱分解が相当に少なく、形成されるポリエステルの非制御架橋を生ずるチタン重縮合触媒を用いる、熱安定で、アンチモンを含まない無彩色のポリエステル類を製造するための方法、および、この方法によって製造される、著しく透明で無彩色な製造物に関する。

【0002】

【従来の技術】

ポリエステルは、極めて多くの使用分野で極めて大きな重要性を有している。

特に、飽和ポリエステル類は、繊維材料の製造に広範に使用され、他のタイプの造形物品、例えば、飲料用のボトルにも使用されている。

これらポリエステル類の押出法による欠点のない加工性および押出物の、例えば、繊維工業または飲料工業におけるさらなる使用のために、極めて高度の要件が、ポリエステル類の品質に課せられている。

特に、特別な加工操作作用に使用されるポリエステルタイプの加工性および使用性は、極めて厳格な制限内で常時同一であることが要求される。

押出法、例えば、溶融紡糸によって加工するためには、なによりもまず、これらが、絶えず均一な分子量と絶えず再現可能な分子量分布とを有し、ゲル画分を含まず、可能な限り、黄変または熱分解しにくいことが重要である。

With thermally stable which Claim 10~18 states at least in one claim, with the polyester of colorless which does not include antimony, in catalytic the inert manganese complex and cobalt complex, phosphorous acid or polyester. which is a complex of the ester

[Claim 20]

With thermally stable which Claim 10~19 states at least in one claim, with the polyester of colorless which does not include antimony, when depending, polyester. which includes crosslinked structure basic 1,000 ppm or less

[Description of the Invention]

【0001】

[Technological Field of Invention]

this invention, reproduction quite being easy, when quite trace addition it does titanium condensation catalyst, quite has fast polymerization rate, titanium condensation catalyst which causes uncontrolled crosslinking of polyester where thermal decomposition is little suitably, is formed is used, with thermally stable, method in order to produce polyesters of colorless which does not include antimony. And, it is produced with this method, colorless it regards product considerably with transparent.

【0002】

[Prior Art]

polyester quite has had large importance with quite many applied field.

Especially, saturated polyester are used by production of fiber material extensively, shaped article item of other type, are used for also the bottle for for example beverage.

For further use in, for example fiber industry or beverage industry of fabricability and the extruded product which do not have deficiency with extrusion of these polyesters, quite high-level requisite, is assigned in quality of polyesters.

Especially, fabricability and use property of polyester type which is used for the one for special fabrication work are usual same while quite strict restricting, it is required.

In order to process with extrusion, for example melt spinning, most first, these, always the uniform molecular weight always have reproducible molecular weight distribution, it does not include gel fraction, possible limit, yellowing or thermal decomposition is difficult to do it is important.

さらなる加工性に対しては、触媒金属が、染色工程中に、可能な限り、繊維材料から溶出しないことである。

何故ならば、これらは、染物屋の廃水からされ、高価な精製操作により廃棄される必要があるからである。

使用済みポリエステル製造物の廃棄または再使用(リサイクル)中の厄介な構成成分によって生ずる困難もまた存在してはならない。

[0003]

ポリエステル類は、通常、芳香族ジカルボン酸の脂肪族ジオールとのエステル化または芳香族ジカルボン酸低級脂肪族エステルの脂肪族ジオールとのエステル交換、および、続く、計画された用途に必要とされる分子量が達成されるまでの重縮合によって製造される。

[0004]

可能なエステル交換は、エステル交換が終了した後、錯形成剤の添加により失活される必要のあるエステル交換触媒の存在で行われる。

通常使用される錯形成剤は、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体である。

エステル化またはエステル交換後、重縮合を行うと、所望の分子量を与え、これは、また、適当な触媒の存在で行われる。

アンチモン化合物、通常は、三酸化アンチモンが、大きな工業的規模で重縮合触媒として受け入れられてきた。

ここで、アンチモン化合物のあるものは、還元剤により還元されて、アンチモン金属となり、これは、ポリエステルの艶消しを生ずる。

これは、透明性を欠き、非無彩色の色相を生ずる。

[0005]

さらに、アンチモン化合物のポリエステル中での比較的高い含量は、その製造を高価なものとするので、欠点と見なされる。

また、さらなる処理操作中、例えば、染色中に、アンチモン化合物が放出される恐れがある。

アンチモン化合物の比較的高い含量は、アンチモン析出物の形成以外に、紡糸性に影響を及ぼす。

Vis-a-vis further fabricability, catalyst metal, in dyeing step, is not to be equated from possible limit, fiber material.

If why is, these to be done from waste water of dyeing thing house, because it is necessary to be abolished by expensive purification operation.

Difficulty which it occurs with cumbersome ingredient in abolition of after use polyester production ones or reuse (recycle) does not have to exist and.

[0003]

polyesters continues, usually, esterification of aliphatic diol of aromatic dicarboxylic acid or ester exchange, of aliphatic diol of aromatic dicarboxylic acid lower fatty ester and, until molecular weight which is needed for application which plan is done is achieved, it is produced with condensation polymerization.

[0004]

As for possible ester exchange, after ester exchange ends, is done in existence of ester exchange catalyst where it is necessary inactivation to be done by the addition of complexing agent.

complexing agent which is used usually phosphoric acid, phosphorous acid and/or phosphonic acid or is those derivative.

When after esterification or transesterification, condensation polymerization is done, it gives desired molecular weight, as for this, in addition, it is done in existence of suitable catalyst.

It was accepted with industrial scale where antimony compound, usually, antimony trioxide, is large as condensation catalyst.

Here, those which have antimony compound being reduced by reductant, become antimony metal, this causes antitarnish of polyester.

This lacks transparency, causes hue of non-colorless.

[0005]

Furthermore, because content where inside of polyester of the antimony compound is high relatively designates production as expensive ones, it is considered deficiency.

In addition, there is a possibility antimony compound being discharged in the further processing operation and during for example dyeing.

content where antimony compound is high relatively, other than forming the antimony precipitate, exerts influence on spinning property.

[0006]

したがって、上記した製造方法の欠点をなくするための提案が、既に、なされている。

[0007]

かくして、コバルト化合物および/または蛍光増白剤の添加により、ポリエステルの色相を改良することが公知である。

さらに、重縮合触媒として、アンチモン化合物の代わりに、チタン化合物を使用することが公知である。

[0008]

種々の刊行物、例えば、US-A-3,962,189、JP-PS-28006(1979)、JP-PS-123,311(1976)、JP-PS-43564(1979)、JP-PS-111985(1980)またはJP-PS-280048(1989)は、ポリエステルの色相を改良するために、エステル交換触媒と同様に、重縮合の開始前に錯形成される必要のあるコバルト化合物を添加し、重縮合をチタン化合物の存在で行う、ポリエステル類を製造するための方法を開示している。

[0009]

これらの刊行物に従えば、添加されるコバルトと錯形成するために使用される錯形成剤の量は、コバルト化合物 1 モル当たり、0.5~7.5 モルの範囲内ということである。

使用される P/Co 比は、かくして、JP 特許 28006 では、0.5~1.5 であり、JP 特許 111985 では、0.7~3 であり、JP 特許 280048 では、0.5~7.5[mol/mol]である。

この公知の方法は、アンチモン化合物の使用に伴う全ての欠点を克服し、かくして、実際に、要求される処理操作および使用に適当な無彩色の透明なポリエステル類を製造することが可能であるというかなりの利点を有する。

しかし、この公知の方法の欠点は、その再現性が幾分不十分なまま残る点である。

かくして、場合によっては、所望される製造物が得られず、代わりに、重縮合反応が妨害され、必要とされる分子量に到達せず、重縮合時間を延長することが必要と考えられる場合には、ポリエステルが黄変し、架橋が制御できないために、ゲル画分が形成され、製造物の感熱性を生じ、さらなる処理を多分に損なう。

したがって、方法それ自体が与える利点は、必ずしも実現されない。

[0006]

Therefore, deficiency of manufacturing method which was inscribed is lost proposition in order to do has done, already.

[0007]

This way, with addition of cobalt compound and/or fluorescent whitener, hue of polyester is improved is public knowledge.

Furthermore, in place of antimony compound, titanium compound is used is public knowledge as condensation catalyst.

[0008]

method in order various publication, for example U.S. Patent-A-3,962,189, JP-PS-28006 (1979), JP-PS-123, 31 1 (1976), JP-PS-43564 (1979), JP-PS-111985 (1980) or JP-PS-280048 (1989), in order to improve hue of polyester, in the same way as ester exchange catalyst, adds cobalt compound where it is necessary complexing to be done before starting condensation polymerization, does condensation polymerization in existence of titanium compound, to produce polyesters is disclosed.

[0009]

If you follow these publication, cobalt and complexing which are added the quantity of complexing agent which is used in order to do is inside range of cobalt compound per mole, 0.5~7.5 mole.

P/Co ratio which is used, with JP patent 28006, with 0.5 - 1.5, with JP patent 111985, with 0.7 - 3, with JP patent 280048, is 0.5 - 7.5 [mol/mol] this way.

This known method overcomes all deficiency which accompanies use of antimony compound, you say that actually, transparent polyesters of suitable colorless is produced is possible in processing operation and use which are required, this way, it possesses considerable benefit.

But, as for deficiency of this known method, reproducibility some insufficient way is the point which remains.

This way, when depending, product which is desired is not acquired, when it is thought, that in substituting, condensation polymerization is done, bogging does not arrive in molecular weight which is needed, condensation polymerization time is extended is needed polyester to do yellowing, gel fraction to be formed because it cannot control crosslinking, heat sensitive of product occurring, Further treatment is impaired much.

Therefore, benefit which that itself of method gives is not always actualized.

[0010]

[発明が解決しようとする課題]

本発明の課題は、再現が極めて容易であり、重縮合触媒を極めて少量添加する場合にも極めて速い重合速度を有し、熱分解が相当少なく、形成されるポリエステルの非制御架橋を生ずる重縮合触媒を用いる、熱安定で、アンチモンを含まない無彩色のポリエステルを製造するための方法、および、この方法によって製造される製造物を提供することである。

[0011]

[課題を解決するための手段]

さて、驚くべきことに、可能なエステル交換を、触媒金属基準で、エステル交換触媒、好ましくは、マンガン化合物の形態のマンガン 20~120ppm の存在で行い、ついで、エステル化またはエステル交換が終了した後、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体を、使用したエステル交換触媒に対する当量の 100%量および使用されるコバルトに対する当量の 99%以下の量、錯形成剤として、エステル化またはエステル交換バッチに加え、コバルト化合物形態のコバルト 0~80ppm をバッチに加え、重縮合を、アンチモンを添加することなく、チタン化合物の形態で添加されるチタン 1~10ppm の存在、ならびに、適当とあらば、架橋構造基を与える有機化合物 1,000ppm 以下、および、適当とあらば、蛍光増白剤 50ppm 以下の存在で行う場合には、芳香族ジカルボン酸の脂肪族ジオールとのエステル化または芳香族ジカルボン酸低級脂肪族エステルの脂肪族ジオールとのエステル交換、および、続く、重縮合によって常時再現可能なように、熱安定で、アンチモンを含まない無彩色のポリエステルを製造することができるが見いだされた。

[0012]

適当なエステル交換触媒は、文献により公知である。

例えば、周期律表の Ia 族(例:Li,Na,K)、IIa 族(例:Mg,Ca)および VIIa 族(例:Mn)の金属化合物、特に、エステル交換バッチで一定の溶解度を有するもの、例えば、有機酸の塩が、本発明に従う方法に対して適当である。

好ましい化合物は、VIIa 族、特に、マンガンの、低級脂肪族カルボン酸塩、特に、酢酸塩である。

[0010]

[Problems to be Solved by the Invention]

problem of this invention, reproduction quite being easy, when quite trace addition it does condensation catalyst, quite has fast polymerization rate, condensation catalyst which causes uncontrolled crosslinking of polyester where thermal decomposition suitable is little, is formed is used, with thermally stable, method in order to produce polyester of colorless which does not include antimony. And, it is to offer product which is produced with this method.

[0011]

[Means to Solve the Problems]

Well, after in surprising fact, possible ester exchange, with catalyst metal standard, is done in existence of manganese 20~120 ppm of morphological form of ester exchange catalyst, preferably, manganese compound, next, esterification or transesterification ends, phosphoric acid, phosphorous acid and/or phosphonic acid or quantity of 99% or less of equivalent for 100% quantity of equivalent for ester exchange catalyst which uses those derivative, and the cobalt which is used, as complexing agent, When existence of titanium 1~10 ppm which is added with morphological form of titanium compound in addition to esterification or transesterification batch, cobalt 0~80 ppm of cobalt compound morphological form in addition to the batch, condensation polymerization, without adding antimony, and, suitability and an organic compound 1,000 ppm or less, and suitability which give mule and crosslinked structure basis. It does in existence of mule and fluorescent whitener 50 ppm or less, Of aliphatic diol of aromatic dicarboxylic acid ester exchange, of esterification or aliphatic diol of the aromatic dicarboxylic acid lower fatty ester and, it continues, with condensation polymerization regular reproducible way, with thermally stable, polyester of colorless which does not include antimony was discovered can be produced.

[0012]

suitable ester exchange catalyst is public knowledge with literature.

Group Ia of for example Periodic Table (Example:Li,Na,K), Group IIa (Example:Mg, Ca) and metal compound, of VGroup IIa (Example:Mn) especially, those which possess fixed solubility with ester exchange batch. salt of for example organic acid, is suitable vis-a-vis method which you follow this invention.

Desirable compound, VGroup IIa, especially, lower fatty carboxylic acid salt of the manganese, especially, is acetic acid salt.

## [0013]

したがって、本発明に従う方法の好ましい実施態様は、可能なエステル交換をマンガン化合物、特に、酢酸マンガ形態の(金属として計算した)マンガ 20~120ppm の存在で行うことを含む。

## [0014]

ポリエステルの色相を改良するために加えられるコバルト化合物は、便宜的に、同様に、コバルトの有機酸塩、例えば、酢酸またはアジピン酸塩である。

コバルト化合物の最小量は、無彩色の色相を達成するために個々の場合に必要とされる色のシフトの度合いに依存する。

蛍光増白剤が色の補正用に追加的に使用される場合には、コバルト化合物の量は、当然のことながら、少なくなる。

一般に、必要とされる添加コバルトの量は、上記の通り、常時ポリエステルの重量基準で、(金属として計算して)50ppm 以下である。

好ましくは、コバルト 20~40ppm は、コバルト化合物の形態で混合物に加えられ、すなわち、遊離のコバルト量 20~40ppm に相当するコバルト化合物の量が増えらる。

## [0015]

従来法におけるように、エステル交換触媒は、重縮合を妨害する、すなわち、必要とされる高分子量が達成できず、さらに得られるポリエステルが熱に暴露した時に粘度が増大するので、本発明に従う方法の重縮合の開始前に、錯形成剤を加えることによって不活性化される。

単離される場合には、重縮合前に添加されるコバルト化合物は、また、製造されるポリエステルの熱安定性を改良するために錯形成される。

## [0016]

本発明に従う方法に対しては、かくして、いかなる条件下でも、添加したコバルト化合物の合計量が不活性化されてはならず、添加コバルト化合物の 1~10%が錯形成されないままであることが不可欠である。

## [0017]

したがって、錯形成剤の量は、錯形成によりエステル交換触媒が 100%失活せず、コバルト化

## [0013]

Therefore, possible ester exchange manganese compound, especially, it does embodiment where method which you follow this invention is desirable, in existenceof (It calculated as metal. ) manganese 20~120 ppm of manganese acetate morphological form it includes .

## [0014]

cobalt compound which is added in order to improve hue of polyester, convenient and in same way, is organic acid salt, for example acetic acid or adipate of the cobalt.

minimum amount of cobalt compound when it is individual in order to achieve the hue of colorless depends on extent of shift of color which is needed.

When fluorescent whitener is used for one for correction of color additional, the quantity of cobalt compound, obvious thing, decreases.

Generally, quantity of addition cobalt which is needed, above-mentioned sort, with weight basis of regular polyester, (Calculating as metal ) is 50 ppm or less.

As for preferably, cobalt 20~40 ppm, it can add quantity of cobalt compound which issuitable to namely, free amount of cobalt 20~40 ppm in addition to blend, with morphological form of the cobalt compound.

## [0015]

In order in prior art method, condensation polymerization bogging it does ester exchange catalyst, the namely, not be able to achieve high molecular weight which is needed, when furthermore polyester which is acquired discloses to heat, because the sensitivity increases, before starting condensation polymerization of method which you follow this invention, complexing agent is added, inactivation it is done by .

When it is isolated, as for cobalt compound which is added before condensation polymerization, in addition, complexing it is done in order to improve thermal stability of the polyester which is produced.

## [0016]

Is added total amount of cobalt compound which being done, inactivation it does not become under any condition this way vis-a-vis method which you follow this invention,, 1 - 10% of addition cobalt compound complexing ね certain it is a essential so far .

## [0017]

Therefore, quantity of complexing agent, ester exchange catalyst 100% inactivation does not dowith complexing , in

合物の 90~99%のみが錯形成されるように選択する。

[0018]

錯形成剤の錯形成力が正確に知られている場合には、コバルトの量に対する当量の錯形成剤の量の 90~99%は、容易に使用することができる。

しかし、一般に、予備実験によって、必要とされる錯形成剤の量を決定することがより多く適当である。

このために、例えば、錯形成剤の理論的に必要とされる量の約 80~120%を重縮合バッチの数回の試験バッチに加え、これら全てを計画した主バッチと同一組成とし、ついで、重縮合を、同一条件下で行う。

重縮合反応が終了した後、達成された粘度(すなわち、達成された分子量)は、全てのバッチで決定する。

このような一連の予備実験の結果は、図面の図 1 に示す。

この場合、到達した粘度は、座標系で、錯形成剤対コバルト化合物の比(例えば、P/Co 比)に対してプロットする。

P/Co 比が大きすぎる場合には、極低い粘度、すなわち、低分子量となることが判明する。

P/Co 比がある限度以下では、達成される分子量は、大きくなる。

曲線の平坦部と上昇分岐との間の変曲点は、当量の P/Co 比を表す。

かくして、錯形成剤の量 99%以下が、ついで、主バッチに加えられる。

[0019]

エステル化またはエステル交換が終了した後、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体が、エステル化もしくはエステル交換バッチに、錯形成剤として、使用されるエステル交換触媒に対する当量の 100%量および使用されるコバルトに対する当量の 90~99%の量加えられる場合には、特に有利である。

[0020]

コバルト化合物を一部のみ失活させる工程は、驚くべきことに、本方法の再現性をドラスチックに改良し、極めて少量のチタン重縮合触媒を加

order only 90 - 99% of cobalt compound complexing to be done, selects.

[0018]

When complexing strength of complexing agent is known accurately, 90 - 99% of the quantity of complexing agent of equivalent for quantity of cobalt you can use, easily.

But, generally, with preparatory experiment, quantity of complexing agent which is needed is decided to be more is suitable.

Because of this, are designated as main batch and same composition which these all plan are done approximately 80 - 120% of quantity which is needed for theoretical of for example complexing agent in addition to test batch of several times of condensation polymerization batch, next, condensation polymerization, is done under the identical condition.

After condensation polymerization ends, it decides viscosity (namely, molecular weight which is achieved) which is achieved, with all batch.

It shows result of this kind of consecutive preparatory experiment, in Figure 1 of drawing.

In this case, with coordinate system, plot it does viscosity which arrives, vis-a-vis ratio (for example P/Co ratio) of complexing agent anti-cobalt compound.

When P/Co ratio is too large, extremely it becomes low viscosity, namely, low-molecular-weight, it is ascertained.

Below limit which has P/Co ratio, molecular weight which is achieved becomes large.

flat part of curve and inflection point between rise branch display P/Co ratio of equivalent.

This way, next, it can add to main batch quantitative 99% or less of complexing agent.

[0019]

After esterification or transesterification ends, phosphoric acid, phosphorous acid and/or phosphonic acid or those derivative, in esterification or the ester exchange batch, 90 - 99% quantity of equivalent for 100% quantity of equivalent for ester exchange catalyst which is used as complexing agent, and cobalt which is used when it is added, especially it is profitable.

[0020]

cobalt compound only part step which inactivation is done, in surprising fact, improves reproducibility of this method to do lath check, condensation polymerization velocity quite

えた場合にも、重縮合速度が極めて速く、熱分解が相当に少なくなり、形成されるポリエステルが架橋が制御されることなく、したがって、黄変およびゲル形成を生じない。

したがって、本発明に従う反応処理法では、美観のための添加剤が少なくすみ、欠点のない加工性が達成される。

得られるポリエステルは、透明度および無彩色性に関しての極めて高品質の要件を満たす。

[0021]

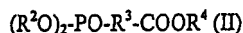
本発明に従う方法に対する適当な錯形成剤は、原理的には、錯形成剤として公知であり、エステル交換触媒用の不活性化剤である全ての化合物である。

リン含有化合物、例えば、リン酸、亜リン酸およびホスホン酸ならびにこれらの誘導体は、特に適当であることが証明されている。

リン酸誘導体の具体的な例は、“PHM エステル類”、すなわち、式 I:



[式中、基  $R^1$  は、同一であっても、異なってもよく、アルキル、ヒドロキシアリルまたはアルコキシ化されたヒドロキシアリル基である。]で表されるオキシアリル化されたアルキル-ヒドロキシアリル-リン酸エステル類、または、式 II:



[式中、 $R^2$ 、 $R^3$  および  $R^4$  は、アルキル基である。]で表されるホスホン酸エステル類の混合物である。

[0022]

チタン化合物は、本発明に従う方法において、重縮合触媒として使用される。

この目的のために既に説明した全てのチタン化合物、特に、カリウムチタニルオキサレートまたはチタニイソプロピレートは、基本的に適当である。

[0023]

アンチモンを加えることなく、ジクロロ酢酸中 25 deg C で測定した固有粘度(IV) 0.4~0.9 dl/g 以下、好ましくは、0.5~0.7 dl/g 以下で、溶融物中でのカルボキシル濃度 10~50 mmol/kg 以下、好ましくは、10~40 mmol/kg 以下で、ついで、固相で所望される最終粘度以下であるチタン 1~10 ppm の存在で重縮合を行うと、特に好ましい。

is quick even with when titanium condensation catalyst of quite trace is added, without crosslinking of polyester where thermal decomposition decreases suitably, is formed being controlled, therefore, yellowing or gel-forming are not caused.

Therefore, with reaction procedure method which you follow this invention, additive for fine appearance may be little, fabricability which does not have deficiency is achieved.

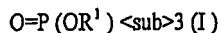
polyester which is acquired in regard to clarity and colorless characteristic fills up requisite of quite high quality.

[0021]

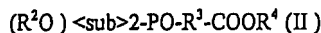
suitable complexing agent for method which you follow this invention, with public knowledge, is all compound which is a inactivation medicine for ester exchange catalyst in principle as the complexing agent.

phosphorus-containing compound, for example phosphoric acid, phosphorous acid and phosphonic acid and these derivative especially are suitable, it is proven.

As for concrete example of phosphoric acid derivative, "pH Mesters", namely, Formula I:



oxy alkylation which is displayed with [In Formula, Group  $R^1$  may differ, being same, alkyl, hydroxyalkyl or it is a hydroxyalkyl group which alkoxylation is done.] alkyl-hydroxyalkyl-phosphate ester which are done, or, Formula II:



It is a blend of phosphonic acid esters which is displayed with [In Formula,  $R^2$ ,  $R^3$  and  $R^4$  are alkyl group.].

[0022]

titanium compound regarding to method which you follow this invention, is used as condensation catalyst.

all titanium compound, which is explained already because of this objective especially, potassium titanyl oxalate or titanium isopropionate is suitable in basic.

[0023]

When inherent viscosity which was measured with 25 deg C in dichloroacetic acid without adding antimony, (IV) with 0.4 - 0.9 dl/g or less, preferably, 0.5~0.7 dl/g or less, below carboxyl concentration 10~50 mmol/kg or less, preferably, 10~40 mmol/kg in the melt, condensation polymerization is done in existence of titanium 1~10 ppm which is below the final viscosity which next, is desired with solid phase, especially it is desirable.



## [0024]

本発明に従うポリエステル類の最終粘度は、上記条件下で測定して、0.7~2.0dl/g、好ましくは、0.7~1.5dl/gの範囲内となるのがよい。

重縮合時間および重縮合温度は、公知の方法で、所望の最終粘度が達成されるように制御される。

一般に、重縮合は、ポリエステルの性質によるが、ポリエステル製造分野で慣用的な方法で行われ、260~350 deg Cで行われ、好ましくは、不活性ガス下、例えば、窒素下、および/または、0.2~10 ミリバール、好ましくは、0.4~5 ミリバールの範囲の減圧下で行われる。

## [0025]

ある種のポリエステルの性質、例えば、熔融粘度を調整するためには、限られた度合いの架橋を生ずることが望ましい。

このために、重縮合は、アンチモンを加えることなく、チタン 2~8ppm の存在中、架橋構造基を与える有機化合物 1,000ppm 以下、好ましくは、100~500ppm の存在で行われる。

## [0026]

使用される架橋剤は、エステルを形成することのできる少なくとも 3 個の官能基を含有する化合物である。

エステルを形成することのできる官能基は、OH 基、カルボキシル基、アルコキシカルボニル基、特に、低級アルコキシカルボニル、カルボン酸無水物基およびこれらから誘導される反応性基である。

慣用的な架橋剤の例は、ペンタエリスリトール、トリメチロールプロパン、トリメリット酸、トリメシン酸(trimesic acid)、ピロメリット酸等である。

## [0027]

ポリエステルの色相をさらに改良し、コバルトを節約するために、アンチモンを加えることなく、蛍光増白剤 50ppm 以下、好ましくは、5~25ppm の存在で重縮合を行うのが適当であることが証明されている。

## [0028]

ポリエステル類の化学組成は、それらの性質に対して極めて重要である。

especially it is desirable.

## [0024]

As for final viscosity of polyesters which you follow this invention, measuring under above-mentioned condition, it is good to be inside range of 0.7- 2.0 dl/g, preferably, 0.7~1.5 dl/g.

condensation polymerization time and condensation polymerization temperature are controlled, in order with known method, for desired final viscosity to be achieved.

Generally, as for condensation polymerization, with property of polyester, in polyester production field is done with usual method, is done with 260 - 350 deg C, is done under preferably, inert gas, under for example nitrogen and under vacuum of range of and/or, 0.2~10 millibar, preferably, 0.4~5 millibar.

## [0025]

In order to adjust property, for example melt viscosity of polyester of a certain kind, crosslinking of extent which is limited is caused, it is desirable.

Because of this, condensation polymerization while existing of titanium 2~8 ppm, is done in existence of organic compound 1,000 ppm or less, preferably, 100~500 ppm which gives crosslinked structure basis without adding the antimony.

## [0026]

As for crosslinking agent which is used, it is a compound which contains functional group of at least 3 which can form ester.

functional group which can form ester, OH group, carboxyl group, alkoxy carbonyl group, especially, lower alkoxy carbonyl, carboxylic acid anhydride group and is reactive group which is induced from these.

Example of usual crosslinking agent, pentaerythritol, trimethylolpropane, trimellitic acid, trimesic acid (trimesic acid), is pyromellitic acid etc.

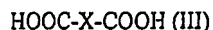
## [0027]

Furthermore it improves hue of polyester, in order to save the cobalt, it is suitable to do condensation polymerization in existence of fluorescent whitener 50 ppm or less, preferably, 5~25 ppm, without adding antimony, it is proven.

## [0028]

chemical composition of polyesters quite is important vis-a-vis those property.

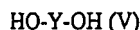
上記意図した用途に適当なポリエステル類を製造するために、本発明に従う方法に対して、上記条件下、式 III:



で表される芳香族ジカルボン酸またはその低級脂肪酸エステル 80~100mol%、および、式 IV:



で表される芳香族ヒドロキシカルボン酸 0~20mol%またはその低級脂肪酸エステルを、式 V:



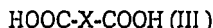
で表されるジオールで、エステル化またはエステル交換する。

この際、X は、ジカルボン酸およびヒドロキシカルボン酸の合計量基準で、5~16 個、好ましくは、6~12 個の炭素原子を有する芳香族基を 80mol%以上、および、4~10 個、好ましくは、6~8 個の炭素原子を有する脂肪族基 20mol%以下であり、X<sup>1</sup> は、p-フェニレン基であり、Y は、エステル交換またはエステル化されたジオールの合計量基準で、2~4 個の炭素原子を有するアルキレンもしくはポリメチレンまたは 6~10 個の炭素原子を有するシクロアルカンもしくはジメチレンシクロアルカン基少なくとも 80mol%、4~16 個、好ましくは、4~8 個の炭素原子を有する直鎖もしくは分岐アルカンジイルまたは式  $-(\text{C}_2\text{H}_4-\text{O})_n-\text{C}_2\text{H}_4-$  (式中、n は、1~40 の整数である) で表される基 20mol%以下であり、n は、好ましくは、20mol%以下の含量に対して、1 または 2 であり、n=10~40 の基が、好ましくは、5mol%未満の含量しか存在しない。

[0029]

X が、ジカルボン酸およびヒドロキシカルボン酸の合計量基準で、p-フェニレン基 90~100mol%、m-フェニレン基 0~7mol%、および、4~10 個、好ましくは、6~8 個の炭素原子を有する脂肪族基 0~5mol%であり、X<sup>1</sup> が、p-フェニレン基であり、Y が、エステル交換またはエステル化されたジオールの合計量基準で、2~4 個の炭素原子を有するアルキレンもしくはポリメチレンまたは 6~10 個の炭素原子を有するシクロアルカンもしくはジメチレンシクロアルカン基少なくとも 90mol%、4~16 個、好ましくは、4~8 個の炭素原子を有する直鎖もしくは分岐アルカンジイルまたは式  $-(\text{C}_2\text{H}_4-\text{O})_n-\text{C}_2\text{H}_4-$  (式中、n は、1 または 2 の数である) で表される基 10mol%以下であるように出発物質を選択すると、特に好ましい。

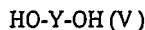
Description above in order to produce suitable polyesters in application which is intended, vis-a-vis method which you follow this invention, under the above-mentioned condition, Formula III:



So aromatic dicarboxylic acid which is displayed or lower fatty ester 80~100 mol%, and Formula IV:



So aromatic hydroxycarboxylic acid 0~20 mol% which is displayed or lower fatty ester, Formula V:



So with diol which is displayed, esterification or transesterification it does.

In this case, as for X, with total amount standard of dicarboxylic acid and the hydroxycarboxylic acid, 5 - 16, aromatic group which possesses carbon atom of preferably, 6~12 80 mol % or more, and, 4 - 10, preferably, 6~8 with aliphatic group 20 mol % or less where has carbon atom; as for X<sup>1</sup>, with p-phenylene group; As for Y, with total amount standard of diol which transesterification or esterification is done, alkylene or polymethylene which possess carbon atom of 2 - 4 or cycloalkane or dimethylene cycloalkane group which possess 6 - 10 carbon atom at least straight or branched alkane diyl or the formula where 80 mol%, 4~16, preferably, 4~8 has carbon atom -  $(\text{C}_2\text{H}_4-\text{O})_n$  -  $\text{C}_2\text{H}_4-$  with group 20 mol % or less which is displayed with (In Formula, n is integer 1 - 40.), as for n, vis-a-vis content of the preferably, 20 mol % or less, with 1 or 2, Basis of n=10~40 exists, only content under preferably, 5 mol%.

[0029]

X, with total amount standard of dicarboxylic acid and hydroxycarboxylic acid, p-phenylene group 90~100 mol%, m-phenylene group 0~7 mol%, and 4 - 10, preferably, 6~8 with aliphatic group 0~5 mol% where has carbon atom; X<sup>1</sup>, with p-phenylene group; As Y, with total amount standard of diol which transesterification or esterification is done, the alkylene or polymethylene which possess carbon atom of 2 - 4 or cycloalkane or dimethylene cycloalkane group which possess 6 - 10 carbon atom at least straight or branched alkane diyl or formula where 90 mol%, 4~16, preferably, 4~8 has carbon atom -  $(\text{C}_2\text{H}_4-\text{O})_n$  -  $\text{C}_2\text{H}_4-$  been a group 10 mol % or less which is displayed with (In Formula, n is quantity of 1 or 2.), when starting substance is selected, especially it is desirable.

## [0030]

本発明に従う方法において、式 IV で表されるヒドロキシカルボン酸を使用せず、式 III で表されるジカルボン酸成分を、X が、ジカルボン酸およびヒドロキシカルボン酸の合計量基準で、p-フェニレン基 93~99mol%、好ましくは、95~98mol%、および m-フェニレン基 1~7mol%、好ましくは、2~5mol%であるように選択すると、特に好ましい。

X および X<sup>1</sup> によって表される芳香族基は、非置換であるか、または、ポリエステルのある種の性質を改質する場合には、1 個または 2 個の置換基を有してもよい。

好ましくは、基は、主として、非置換であり、すなわち、芳香族基の 10mol%以下が、置換基を有する。

置換基の正確な含量は、達成される効果に従い特異的である。

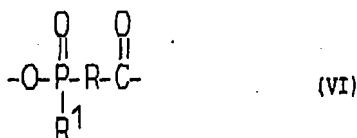
好ましい可能な置換基は、メチル基およびスルホン基である。

## [0031]

ある種の特異的な性質が所望される場合には、上記出発物質以外に、他の共縮合可能な化合物 10mol%以下、好ましくは、7mol%以下が、ポリエステルに共縮合可能である。

例えば、易燃性の低いポリエステルは、共縮合されるジカルボン酸、および、適当な場合には、ヒドロキシカルボン酸の全量基準で、式 VI:

## [化 3]



[式中、R は、飽和開放鎖または環式アルキレン、アリーレンまたはアラールキレン基、好ましくは、2~6 個の炭素原子を有するアルカンジイル、2~6 個の炭素原子を有するシクロアルカンジイル、メチレンフェニルまたはフェニレン、特に、エチレンであり、R<sup>1</sup> は、6 個以下の炭素原子を有するアルキル基またはアリールもしくはアラールキル基、好ましくは、1~6 個の炭素原子を有するアルキル、6~7 個の炭素原子を有するアリールもしくはアラールキル、特に、メチル、エチル、フェニルまたはベンジルである。]で表されるポリエステル構造基を与える、DE-C-23 46 787 および

## [0030]

Regarding to method which you follow this invention, when you do not use hydroxycarboxylic acid which is displayed with Formula IV, as dicarboxylic acid component which is displayed with Formula III, X, with total amount standard of the dicarboxylic acid and hydroxycarboxylic acid, been a p-phenylene group 93~99 mol%, preferably, 95~98 mol%, and a m-phenylene group 1~7 mol%, preferably, 2~5 mol%, you select, especially it is desirable.

aromatic group which is displayed with X and X<sup>1</sup> is the unsubstituted, or when or, property of kind which has polyester is improved, it is possible to possess substituent of 1 or 2.

As for preferably, basis, with unsubstituted, 10 mol % or less of namely, aromatic group, have the substituent mainly.

correct content of substituent is specific in accordance with effect which is achieved.

Desirable possible substituent is methyl group and sulfone group.

## [0031]

When specific property of a certain kind is desired, other than the above-mentioned starting substance, other cocondensable compound 10 mol % or less, preferably, 7 mol % or less, is cocondensable in polyester.

As for polyester where for example easily combustible is low, in case of dicarboxylic acid, and the suitable which cocondensation are done, with total amount standard of hydroxycarboxylic acid, the Formula VI:

## [Chemical Formula 3]

polyester structural group which is displayed with [In Formula, as for R, cycloalkane diyl, methylene phenyl or phenylene, which possesses carbon atom of alkane diyl, 2~6 which possesses carbon atom of saturation open chain or cyclic alkylene, arylene or aralkylene group, preferably, 2~6 especially, with ethylene, as for R<sup>1</sup>, aryl or aralkyl, which possess carbon atom of the alkyl, 6~7 which possesses carbon atom of alkyl group or aryl or aralkyl group, preferably, 1~6 which possesses carbon atom of 6 or fewer especially, it is a methyl, ethyl, phenyl or benzyl.] is given, when with DE-C-23 46 787 and 2,454,189 cocondensation it does compound 1~10 mol% of public

24 54 189によって公知の化合物1~10mol%をポリエステルに共縮合する場合に、本発明に従う方法によって製造することができる。

## [0032]

10 重量%以下の改質剤、充填剤、顔料、染料、抗酸化剤、加水分解、光および熱安定剤および/または加工助剤が、チタン触媒を抑制しない場合には、これらをエステル化、エステル交換または重縮合バッチに加えることができる。

加水分解および熱分解に対して混合物のポリエステル含量を保護するポリエステル安定化剤 10 重量%以下、好ましくは、5 重量%以下の添加は、本発明に従う方法において、特に好ましい。

特に有用な安定化剤は、ポリエステルの末端カルボキシル基と反応して、酸でない末端基、例えば、グリシジルエーテル類、ケテンイミン類、アジリジン類またはイソシアネート類を与える化合物である。

特に有用な安定化剤は、特に、これらを相互に組み合わせて使用する場合には、カルボジイミド類およびポリカルボジイミド類である。

## [0033]

本発明は、上記方法によって製造することができ、芳香族ジカルボン酸および脂肪族ジオールを基体とし、艶消しなしの状態、それらの色数成分が、

a\* -3~+3 の範囲、好ましくは、-2~+2 の範囲

b\* -6~+6 の範囲、好ましくは、-3.5~+3.5 の範囲、および、

L\* 55~75 の範囲、好ましくは、60~70 の範囲である。

## [0034]

本発明に従うポリエステルは、さらに、アンチモンを含まず、(金属として計算して)チタン 1~10ppm、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体との触媒的に不活性な錯体形態のエステル交換触媒金属 20~120ppm、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体との触媒的に不活性な錯体形態で一部存在する(金属として計算して)コバルト 0~80ppm、および、場合によっては、蛍光増白剤 50ppm 以下を含むことを特徴とする。

## [0035]

knowledge in polyester, it can produce with method which you follow this invention.

## [0032]

When modifier, filler, pigment, dye, antioxidant, hydrolysis, light and heat stabilizer and/or processing aid of 10 weight % or less, titanium catalyst is not controlled, these it adds to esterification, ester exchange or condensation polymerization batch, it is possible.

Addition of polyester stabilizer 10 weight % or less, preferably, 5 weight % or less which protects polyester content of blend vis-a-vis hydrolysis and thermal decomposition regarding to method which you follow the this invention, especially is desirable.

Especially useful stabilizer, reacting with carboxyl endgroup of polyester, end group, for example glycidyl ethers, ketene imine and aziridine which are not an acid or is compound which gives the isocyanates.

Especially useful stabilizer when you use especially, combining these with mutual, is carbodiimide and poly carbodiimide.

## [0033]

Produces this invention, with above-mentioned method to be possible, to designate aromatic dicarboxylic acid and aliphatic diol as substrate, with the state of antitarnish none, those color number component,

Range of a\* -3~+3 and range of preferably, -2~+2

Range of b\* -6~+6 and range of preferably, -3.5~+3.5, and,

It is a range of L\* 55~75 and a range of preferably, 60~70.

## [0034]

polyester which you follow this invention, furthermore, does not include antimony, in catalytic of (Calculating as metal) titanium 1~10 ppm, phosphoric acid, phosphorous acid and/or phosphonic acid or those derivative in catalytic ester exchange catalyst metal 20~120 ppm, phosphoric acid, phosphorous acid and/or phosphonic acid of inert complex morphological form or those derivative with inert complex morphological form part (Calculating as metal) cobalt 0~80 ppm, and when it exists depending, includes fluorescent whitener 50 ppm or less, it makes feature.

## [0035]

好ましくは、本発明に従うポリエステルは、アンチモンを含まず、(金属として計算して)チタン 2~8ppm、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体との触媒的に不活性な錯体形態の(金属として計算した)マンガン 50~90ppm、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体との触媒的に不活性な錯体形態で一部存在するコバルト 20~40ppm、および、場合によっては、蛍光増白剤 25ppm 以下を含む。

#### [0036]

コバルトの 90~99%が、リン酸、亜リン酸および/またはホスホン酸あるいはそれらの誘導体との触媒的に不活性な錯体形態であり、それが蛍光増白剤 5~25ppm を含むのがさらに好ましい。

エステル交換触媒、好ましくは、マンガンおよびコバルトの触媒的に不活性な錯体は、原理的には、これらの金属を不活性化するための公知の全ての錯形成剤を含む。

エステル交換触媒、特に、マンガンおよびコバルトの、リン酸、ポリリン酸、または、特に、亜リン酸もしくはその誘導体、とりわけ、これらの酸のエステルとの触媒的に不活性な錯体が好ましい。

ポリエステル鎖の構造も、また、当然のことながら、技術的特徴の全てに対して特に重要である。

純粋に定量的には、それは、公知の繊維形成ポリエステル類に慣用的な構造基から形成されるのがよい。

#### [0037]

これらは、主として、換言すれば、少なくとも 80mol%は、芳香族ジカルボン酸と脂肪族ジオールとから誘導される単位を含む。

慣用的な芳香族ジカルボン酸単位は、ベンゼンジカルボン酸、特に、テレフタル酸およびイソフタル酸の二価の基であり、慣用的なジオールは、2~4 個の炭素原子を有し、エチレングリコールが、特に適当である。

改質ポリエステル類は、好ましくは、少なくとも 80mol%のエチレンテレフタレート単位を含む。

この時、残る 20mol%は、ジカルボン酸単位およびグリコール単位から形成され、これは、いわゆる改質剤として機能し、熟練者であれば、これを制御させて、ポリエステルより製造される製造物、例えば、フィラメントおよび包装材料(例えば、飲料ボトル)の物理的および化学的性質に

影響を及ぼすように設計される。

polyester which you follow preferably, this invention does not include antimony, the catalytic of (Calculating as metal) titanium 2~8 ppm, phosphoric acid, phosphorous acid and/or phosphonic acid or those derivative in catalytic in (It calculated as metal.) manganese 50~90 ppm, phosphoric acid, phosphorous acid and/or phosphonic acid of inert complex morphological form or those derivative with inert complex morphological form part cobalt 20~40 ppm, and when it exists depending, includes fluorescent whitener 25 ppm or less.

#### [0036]

90 - 99% of cobalt, phosphoric acid, phosphorous acid and/or phosphonic acid or with inert complex morphological form, that including the fluorescent whitener 5~25 ppm furthermore is desirable in catalytic of those derivative.

inert complex includes all complexing agent of public knowledge in order inactivation to these metal, to principle in catalytic of ester exchange catalyst, preferably, manganese and cobalt.

ester exchange catalyst, especially, phosphoric acid, polyphosphoric acid, of manganese and cobalt or, especially, phosphorous acid or its derivative, especially, inert complex is desirable in catalytic of ester of these acid.

structure of polyester chain, in addition, obvious thing, especially it is important vis-a-vis all of technical feature.

Purely as for that, it is formed to fiber formation polyesters of public knowledge from the usual structural group is good to quantitative.

#### [0037]

If as for these, you rephrase mainly, at least 80 mol% include the unit which is induced from aromatic dicarboxylic acid and aliphatic diol.

As for usual aromatic dicarboxylic acid unit, benzene dicarboxylic acid, especially, as for usual diol, it possesses carbon atom 2 - 4 with bivalent group of terephthalic acid and isophthalic acid, ethyleneglycol, especially is suitable.

improved polyester preferably, include ethylene terephthalate unit of 80 mol% at least.

If this time, 20 mol% which remain are formed from dicarboxylic acid unit and the glycol unit, this functions and as so-called modifier it is a expert, controlling this, influence and is possible to physical and chemical property of the product, for example filament and packaging material (for example beverage bottle) which are produced from polyester.

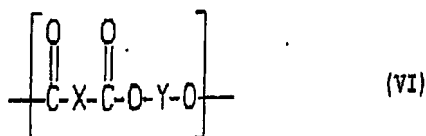
影響を及ぼさせることができる。

このようなジカルボン酸の例は、イソフタル酸基または脂肪族ジカルボン酸基、例えば、グルタル酸、アジピン酸およびセバシン酸基であり、機能を改質するジオール基の例は、長鎖のジオール類、例えば、プロパンジオールまたはブタンジオールの化合物であり、ジ-またはトリエチレングリコールのジオールであり、少量存在する場合には、分子量約500-2,000を有するポリグリコールである。

[0038]

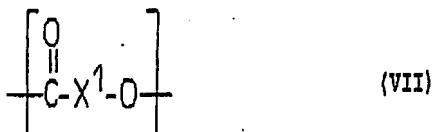
詳細には、本発明に従う好ましいポリエステル類は、そのポリマー鎖が、式 VI:

[化 4]



で表される構造基 80~100mol%、および、式 VII:

[化 5]



で表される構造基 20~0mol%から形成され、上記式中、X が、5~16 個、好ましくは、6~12 個の炭素原子を有する芳香族基 80mol%以上、4~10 個の炭素原子、好ましくは、6~8 個の炭素原子を有する脂肪族基 20mol%以下であり、X<sup>1</sup> が、p-フェニレン基であり、Y が、2~4 個の炭素原子を有するアルキレンもしくはポリメチレンまたは 6~10 個の炭素原子を有するシクロアルカンもしくはジメチレンシクロアルカン基少なくとも 80mol%、および、4~16 個、好ましくは、4~8 個の炭素原子を有する直鎖もしくは分岐アルカンジイルまたは式-(C<sub>2</sub>H<sub>4</sub>-O)<sub>n</sub>-C<sub>2</sub>H<sub>4</sub>-(式中、n は、1~40 の整数である)で表される基 20mol%以下であり、n は、好ましくは、20mol%以下の含量に対して、1 または 2 であり、n=10~40 の基は、好ましくは、5mol%未満の含量でしか存在しないポリエステルである。

[0039]

本発明に従う特に好ましいポリエステルは、p-フ

As for example of this kind of dicarboxylic acid,; as for example of diol group which improves performance, when with diols, for example propanediol of long chain or the compound of butanediol, with diol of di- or triethylene glycol, the trace it exists, it is a polyglycol which molecular weight approximately possesses 500 - 2,000 in isophthalic acid basis or aliphatic dicarboxylic acid group, for example glutaric acid, adipic acid and sebacic acid basis.

[0038]

As for desirable polyesters where in detail, you follow this invention, the polymer chain, Formula VI:

[Chemical Formula 4]

So structural group 80~100 mol%, and Formula VII: which are displayed

[Chemical Formula 5]

aromatic group 80 mol % or more, 4~10 which so is formed from structural group 20~0 mol% which is displayed, in the above Formula, X, 5 - 16, possesses carbon atom of preferably, 6~12 carbon atom, preferably, 6~8 with aliphatic group 20 mol % or less where has carbon atom; X<sup>1</sup>, with p- phenylene group ; Y, alkylene or polymethylene which possess carbon atom of 2 - 4 or cycloalkane or dimethylene cycloalkane group which possess 6 - 10 carbon atom at least 80 mol%, and, 4 - 16, straight or branched alkane di yl or formula where preferably, 4~8 has carbon atom -(C<sub>2</sub>H<sub>4</sub>-O) <sub>n</sub>-C<sub>2</sub>H<sub>4</sub>- with group 20 mol % or less which is displayed with (In Formula, n is integer 1 - 40. ), as for the n, vis-a-vis content of preferably, 20 mol % or less, with 1 or 2, Basis of n=10~40 is polyester which does not exist with only the content under preferably, 5 mol%.

[0039]

Especially as for desirable polyester where you follow this

エニレン基 90~100mol%、m-フェニレン基 0~7mol%、および、4~10 個、好ましくは、6~8 個の炭素原子を有する脂肪族基 0~5mol%であり、Y が、2~4 個の炭素原子を有するアルキレンもしくはポリメチレンまたは 6~10 個の炭素原子を有するシクロアルカンもしくはジメチレンシクロアルカン基少なくとも 90mol%、および、4~16 個、好ましくは、4~8 個の炭素原子を有する直鎖または分岐アルカンジイルまたは式  $-(C_2H_4-O)_n-C_2H_4-$  (式中、n は、1 または 2 の数である) で表される基 10mol% 以下である、式 IV で表される構造機によって構成されるポリエステルである。

[0040]

本発明に従うとりわけ好ましいポリエステル類は、式中、X が、p-フェニレン基 93~99mol% および m-フェニレン基 1~7mol% である、式 IV で表される構造基によって構成されるポリエステルである。

[0041]

ポリエステルの架橋の限られた度合いを確立することが適当である場合が多い。

これらの場合には、ポリエステルが 1,000ppm 以下の上記架橋構造基を含むことが好ましい。

[0042]

溶融重合によって製造される本発明に従うポリエステルは、便宜上、ジクロロ酢酸中 25 deg C で測定して、固有粘度 (IV) 0.600~0.900 を有する。

[0043]

式 VII で表される構造基を含有するポリエステルは、式 VI で表される構造基 70~100mol%、特に、85~100mol% と、式 VII で表される構造基 0~30mol%、特に、0~15mol% とを含有する。

[0044]

X によって表される芳香族基は、付与された定義のコンテキスト中で、全て、同一であってもよく、あるいは、これらは、異なってもよい。

特に、少なくとも 80mol% 程度、ポリエステル鎖を形成する X によって表される上記構造基は、ポリエステル鎖中に、個々に存在してもよく、混合物として存在してもよい。

80mol% のポリエステル鎖の最小量がこれらの主成分に対して記載した基の群から 1 個または

invention, the p-phenylene group 90~100 mol%, m-phenylene group 0~7 mol%, and 4 - 10, preferably, 6~8 with aliphatic group 0~5 mol% where has carbon atom; Y, alkylene or polymethylene which possess carbon atom of 2 - 4 or cycloalkane or dimethylene cycloalkane group which possess 6 - 10 carbon atom at least 90 mol%, and, 4 - 16, straight chain or branch alkane diyl or formula where preferably, 4~8 has carbon atom  $-(C_2H_4-O)_n-C_2H_4-$  is group 10 mol % or less which is displayed with (In Formula, n is quantity of 1 or 2.), it is a polyester which consists of structure machine which is displayed with Formula IV.

[0040]

As for especially desirable polyesters where you follow this invention, in Formula, X, is p-phenylene group 93~99 mol% and m-phenylene group 1~7 mol%, it is a polyester which is formed with structural group which is displayed with Formula IV.

[0041]

Establishes extent where crosslinking of polyester is limited when it is suitable is many.

In these cases, polyester includes above-mentioned crosslinked structure basis of 1,000 ppm or less, it is desirable.

[0042]

polyester which you follow this invention which is produced with melt condensation polymerization, measuring with 25 deg C in for convenience and dichloroacetic acid, inherent viscosity (IV) has 0.600 - 0.900.

[0043]

polyester which contains structural group which is displayed with Formula VII, structural group 70~100 mol%, which is displayed with Formula VI especially, 85 - 100 mol% and structural group 0~30 mol%, which is displayed with Formula VII especially, contains 0- 15 mol%.

[0044]

aromatic group which is displayed with X, in context of the definition which is granted, may be all, same, or, these may differ.

Especially, above-mentioned structural group which is displayed with the X which at least forms 80 mol% extent, polyester chain may exist in polyester chain, individually, as blend to exist is possible.

minimum amount of polyester chain of 80 mol% when from group of basis which is stated vis-a-vis these main component

2 個の個体のみによって形成される場合が好ましい。

この時、望ましいポリエステル鎖のさらなる改質は、好ましくは、X によって表される存在する 20mol% の構造基の最大量に対して付与された定義のコンテキスト中で他の構造基によって行われる。

[0045]

かくして、80 重量%の芳香族基の最小量は、例えば、全て、1,4-フェニレン基であってもよい、または、これらは、例えば、1,4-フェニレン基:1,3-フェニレン基のモル比 95:5~99:1、または、2,6-ナフチレン基:ビフェニル-4,4'-ジイル基のモル比 4:6~6:4 で構成されてもよい。

好ましいポリエステルは、X が少なくとも 95mol% の芳香族基および 5mol% 以下の脂肪族基であるポリエステル、特に、X が全て芳香族基であるポリエステルである。

[0046]

Y によって表される基も、また、付与された定義のコンテキスト中で、全て、同一であってもよく、あるいは、これらは、異なってもよい。

特に、少なくとも 80mol% 程度、ポリエステル鎖を形成する Y によって表される上記構造基は、ポリエステル鎖中に、個々に存在してもよく、混合物として存在してもよい。

80mol% のポリエステル鎖の最小量がこの主成分に対して記載した基の群から 1 個または 2 個の個体によってのみ形成される場合が好ましい。

この時、望ましいポリエステル鎖のさらなる改質は、好ましくは、Y によって表される存在する 20mol% の構造基の最大量に対して付与された定義のコンテキスト中で他の構造基によって行われる。

かくして、80 重量%の脂肪族基の最小量は、例えば、全て、エチレン基であってもよい、または、これらは、例えば、エチレン基:1,4-ジメチレン-シクロヘキサン基のモル比 10:1~1:10 によって構成されてもよい。

Y が少なくとも 95mol% のエチレン基であるポリエステルが、特に好ましい。

[0047]

X によって表される好ましい芳香族基は、1,4-フェニレンおよび 1,3-フェニレンである。

is formed with only solid of 1 or 2 it is desirable.

In context of definition which is granted vis-a-vis maximum amount of structural group of 20 mol% where this time, further improvement of the desirable polyester chain is displayed with preferably, X and exists it is done with other structural group.

[0045]

This way, minimum amount of aromatic group of 80 weight% is good even with the for example all, 1, 4- phenylene group, or or, these may be constituted, mole ratio 95:5~99:1, of for example 1, 4- phenylene group:1, 3- phenylene group or, 2 and 6 -naphthylene group; biphenyl-4, 4'-diyl group with mole ratio 4:6~6:4.

Desirable polyester polyester, where X at least is aromatic group of 95 mol% and aliphatic group of 5 mol % or less especially, is polyester where the X is all aromatic group.

[0046]

Is displayed with Y, in addition, in context of the definition which is granted, it is possible to be all, same, or, these may differ, group

Especially, above-mentioned structural group which is displayed with the Y which at least forms 80 mol% extent, polyester chain may exist, in polyester chain, individually, as blend to exist is possible.

minimum amount of polyester chain of 80 mol% when with only solid of 1 or 2 it is formed it is desirable from group of basis which is stated vis-a-vis this main component.

In context of definition which is granted vis-a-vis maximum amount of structural group of 20 mol% where this time, further improvement of the desirable polyester chain is displayed with preferably, Y and exists it is done with other structural group.

This way, minimum amount of aliphatic group of 80 weight% is good even with the for example all, ethylene group, or or, these may be constituted with mole ratio 10:1~1:10 of for example ethylene group:1, 4- dimethylene-cyclohexane group.

polyester where Y is ethylene group of 95 mol% at least, especially is desirable.

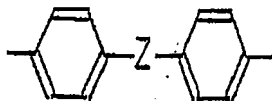
[0047]

Desirable aromatic group where it is displayed with X is, 1 and 4-phenylene and 1 and 3 -phenylene.



しかし、1,4-ナフチレン、1,5-ナフチレン、1,8-ナフチレン、2,6-ナフチレンおよび 2,7-ナフチレン、4,4'-ビフェニレン、フリレン、ならびに、式 VI:

【化 6】



[式中、Z は、1-4 個の炭素原子を有するポリメチレンまたはアルキレン、-SO<sub>2</sub>-、-COO-、-O-、または-S-である。]で表される基も、また、適当な基である。

【0048】

X によって表される芳香族基は、また、1 個または 2 個の置換基を有してもよい。

しかし、この場合、置換される存在する芳香族基 15%以下の含量のみが好ましく、特に、7%以下の含量が好ましい。

好ましくは、各々の場合の置換芳香族基は、1 個の置換基を有するのみである。

特に適当な置換基は、1-4 個の炭素原子を有するアルキル、1-4 個の炭素原子を有するアルコキシ、塩素およびスルホ基である。

【0049】

脂肪族ジカルボン酸と角度をなした鎖を付与する芳香族基、例えば、イソフタル酸基を与えるか、または、より嵩高い芳香核、例えば、ナフタレン核を含有する芳香族基とから誘導される基および Y によって表される長鎖構造基は、特に、ポリエステル改質が望ましい場合に、ポリエステルに組み込まれる。

改質作用を有するこれらの成分 7%未満を含有するポリエステルが好ましい。

【0050】

特別の使用性質を達成するためには、例えば、スルホ基を含有する単位(例えば、スルホ-イソフタル酸)をポリエステルに配合し、それにより、塩基性染料に対する親和性を獲得したり、上記式 VI で表される構造基を配合して、ポリエステルを難燃性とすることもできる。

【0051】

【実施例】

実施例

But, 1 and 4 -naphthylene, 1,5-naphthylene, 1,8-naphthylene, 2,6-naphthylene and 2 and 7 -naphthylene, 4,4'-biphenylene, furylene, and, Formula VI:

[Chemical Formula 6]

(VI)

group which is displayed with [In Formula, Z is polymethylene or alkylene, -SO<sub>2</sub>-, -COO-, -O-, or -S- where it possesses carbon atom 1 - 4. ], in addition, it is a suitable basis.

【0048】

As for aromatic group which is displayed with X, in addition, it is possible to possess substituent of 1 or 2.

But, in this case, is substituted only content of aromatic group 15 % or less which exists to be desirable, especially, content of 7% or less is undesirable.

substituted aromatic group in each case of preferably, is only possesses substituent of 1.

Especially suitable substituent is alkoxy, chlorine and sulfo group which possess the carbon atom of alkyl, 1-4 which possesses carbon atom 1 - 4.

【0049】

aromatic group, for example isophthalic acid basis which grants chain which forms aliphatic dicarboxylic acid and the angle is given, or or, from long chain structural group which is displayed with the group and Y which are induced from aromatic group which contains bulky aromatic nucleus, for example naphthalene nucleus, when especially, improvement of polyester is desirable, is installed in polyester.

polyester which contains under these component 7% which possess improvement action is desirable.

【0050】

In order to achieve special use property quality, combining structural group where it combines unit (for example sulfo-isophthalic acid) which contains for example sulfo group to polyester, acquires affinity for basic dye, with that, is displayed with the above Formula VI, it is possible also to designate polyester as flame resistance.

【0051】

[Working Example(s)]

実施例	1a
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Working Example(s)	1 a
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5kg、ジメチルイソフタレート 0.25kg、エチレングリコール 6kg および酢酸マンガン・ $4\text{H}_2\text{O}$  (ポリエステル基準でマンガン 68ppm) を充填し、攪拌および不活性ガスとしての窒素下、混合物を 140 deg C に加熱する。

4 時間の間に、反応温度を 230 deg C に上昇させ、開裂したメタノールと過剰のエチレングリコールとを留去する。

ついで、溶融反応生成物を重縮合容器に移し、錯形成剤としての  $\text{H}_3\text{PO}_3$  1.65g (165ppm) および酢酸コバルト 1.27g (127ppm) (Co30ppm に相当) を加え、混合物を、230 deg C で、10~15 分間攪拌する。

しかる後、カリウムチタニルオキサレート 0.27g (27ppm) ( $\text{Ti}$  3.6ppm に相当) を加え、このバッチを窒素下 240 deg C で攪拌し、幾分減圧にして、エチレングリコールを留去する。

ついで、1 時間の間に、初期圧を 1.13 ミリバールに低下させ、その間、溶融物の温度は、240 deg C から 270 deg C に上昇する。

ついで、さらに 30 分の間に、温度を 280 deg C に上昇させ、溶融物の試料が、溶融物 1g のジクロロ酢酸 100ml 溶液中 25 deg C で測定して、比溶液粘度 0.83 を有するまで、攪拌を継続する。

これとは別に、さらに便宜的には、重縮合は、また、溶液粘度 0.83 に相当する 280 deg C での溶融物粘度が予備実験で決定される場合には、一定の溶融物粘度まで継続させる。

#### [0052]

溶融物は、冷却し、慣用的な方法で加工して、径 2~3mm を有するペレットとする。

かくして得られたポリエステルは、以下の特性値:

5 kg, dimethyl isophthalate 0.25 kg, ethyleneglycol 6 kg and manganese acetate \*  $4\text{H}_2\text{O}$  (With polyester standard manganese 68 ppm) it is filled, under nitrogen as agitation and inert gas, it heats blend to 140 deg C.

Between 4 hours, it removes ethyleneglycol of methanol and excess which rising in 230 deg C, cision do reaction temperature.

Next, melt reaction product is moved to condensation polymerization container, blend, with 230 deg C, 10 - 15 min is agitated  $\text{H}_3\text{PO}_3$  1.65g as complexing agent (165 ppm) and including cobalt acetate 1.27g (127 ppm) (Suitable to Co 30 ppm).

After that, this batch is agitated with 240 deg C under nitrogen including potassium titanyl oxalate 0.27g (27 ppm) (Suitable to  $\text{Ti}$  3.6 ppm), ethyleneglycol is removed somewhat to vacuum.

Next, between 1 hour, initial pressure decreasing to 1.13 millibar, at that time, temperature of melt from 240 deg C rises in 270 deg C.

Next, furthermore between 30 min, temperature rising in 280 deg C, the sample of melt, with 25 deg C in dichloroacetic acid 100 ml solution of melt 1g measuring, until it possesses ratio solution viscosity 0.83, it continues agitation.

Separately from this, furthermore convenient, as for condensation polymerization, in addition, melt viscosity with 280 deg C which are suitable to solution viscosity 0.83 being preparatory experiment, when it is decided, it continues to fixed melt viscosity.

#### [0052]

It cools melt, processes with usual method, it makes pellet which possesses diameter 2 - 3 mm.

As for polyester which it acquires in this way, property value: below

カルボキシル基含量 [mmol/kg]: 12			
carboxyl group content [mmol/kg]: 12			
ジエチレングリコールの含量 [%]	0		5
content of diethylene glycol [%]	0		5

3.09

3.09

を有する。

[0053]

かくして、製造されたポリエステルは、固相縮合によって、さらに縮合することができる。

このために、上記製造したペレットは、緩やかに全体を混合して、慣用的な方法で、減圧または窒素下、220 deg C で 17 時間加熱する。

上記のように測定した比粘度 1.014 を有するポリエステルが、かくして、得られる。

[0054]

実施例 1b~1l

実施例 1a に記載したように、不連続様式で(実施例 1j~1l)、または、連続操作下で類似した様式で(実施例 1b~1i)、上記実施例を数回繰り返す、個和得たコバルトの量、錯形成剤の性質および量、ならびに、チタン触媒の性質および量を改良し、場合によっては、市販されている蛍光増白剤 [hOECHST AG の登録商標 HOSTALUX KS) または架橋剤ペンタエリスリール) をさらに加えた。溶融物での重縮合は、種々の圧力下および種々の反応時間で行い、縮合の時間および温度は、固相縮合に対しては、変化させた。バッチの組成および反応条件は、変更され、色数および到達する比粘度、ならびに、ポリエステル中のカルボン酸基およびジグリコールの含量は、以下の表 1 および表 2 に記載する。]

[0055]

表中で使用する略号は、以下の意味:

KTi=カリウムチタニルオキサレート; Tiip=イソプロピルチタネート; Co(AcO)<sub>2</sub>·4H<sub>2</sub>O=酢酸コバルト 4 水和物

PO<sub>3</sub>=亜リン酸; PO<sub>4</sub>=リン酸; PPA=ポリリン酸; PHM=PHM エステル

HLX=登録商標 HOSTALUX KS; Penta=ペンタエリスリール

SV=比粘度

[COOH]カルボキシル末端基濃度; DEG=ジエステルグリコールの濃度を有する。

[0056]

ppm データは、全て、バッチで得られるポリエステルの理論量に関する。

加える化合物が金属化合物(例えば、触媒)であ

It possesses.

[0053]

This way, with solid phase condensation, furthermore it can condense the polyester which is produced.

Because of this, description above mixing entirely leniently, with usual method, under vacuum or nitrogen, 17 hours it heats the pellet which is produced, with 220 deg C.

As description above polyester which possesses specific viscosity 1.014 which was measured, is acquired this way.

[0054]

Working Example 1b~1l

As stated in Working Example 1a, fluorescent whitener where with discontinuous style (Working Example 1j~1l), or, (Working Example 1b~1i), several times it repeats above-mentioned Working Example with style which resembles under continuous operation, harmony quantity of cobalt which is acquired, improves property and quantity of property and the quantity, and titanium catalyst of complexing agent, when depending, is marketed [registered trademark HOST ALUX KS) or crosslinking agent pentaerythritol) of hOECH ST AG furthermore was added. It did condensation polymerization with melt, under various pressure and with various reaction time, time of condensation and temperature changed vis-a-vis solid phase condensation. composition and reaction condition of batch are modified, color number and state carboxylic acid group in specific viscosity, and polyester which arrive and content of the diglycol, in Table 1 and Table 2 below. ]

[0055]

As for code which is used with in the table, meaning below:

KTi=potassium titanyl oxalate; Tiip=isopropyl titanate; Co(AcO)<sub>2</sub>·4H<sub>2</sub>O=cobalt acetate tetrahydrate

PO<sub>3</sub>=phosphorous acid; PO<sub>4</sub>=phosphoric acid; PPA=polyphosphoric acid; pH M=pH Mester

HLux=registered trademark HOST ALUX KS; Penta=pentaerythritol

SV=specific viscosity

It possesses concentration of [COOH] carboxyl endgroup concentration; DEG=diester glycol.

[0056]

ppm data regards theoretical amount of polyester which is acquired with the all, batch.

When compound in addition is metal compound (for example

る場合には、化合物の略号は、ppm データが化合物の量を表し、金属記号が与えられている場合には、ppm データは、添加された化合物に含まれる金属の量を表す。

[0057]

[表 1]

catalyst), as for code of compound, ppm data displays quantity of compound, when metal signal is given, ppm data displays quantity of metal which is contained in the compound which is added.

[0057]

[Table 1]

表 1

実施例 番号	重縮合触媒		コバルト化合物			錯形成剤		さらなる添加剤	
	性質	量	性質	量	量	性質	量	性質	量
	(ppm)		(ppm)	(%)	遊離	(ppm)		(ppm)	
		合計			合計				
1b	KTi	27	Co(Ac) <sub>2</sub>	84	0	PO <sub>3</sub>	150	-	-
1c	KTi	27	Co(Ac) <sub>2</sub>	84	0	PO <sub>3</sub>	150	HLUX	10
1d	KTi	27	Co(Ac) <sub>2</sub>	127	0	PO <sub>3</sub>	165	HLUX	10
1e	KTi	27	Co(Ac) <sub>2</sub>	127	0	PO <sub>3</sub>	165	Penta	200
1f	KTi	54	Co(Ac) <sub>2</sub>	127	0	PO <sub>3</sub>	165	-	-
1g	KTi	54	Co(Ac) <sub>2</sub>	169	0	PO <sub>3</sub>	189	-	-
1h	KTi	27	Co(Ac) <sub>2</sub>	127	100	PO <sub>3</sub>	121	-	-
1i	Sb <sub>2</sub> O <sub>3</sub>	395	-	-	-	PO <sub>3</sub>	121	-	-
1j	KTi	45	Co(Ac) <sub>2</sub>	135	10	PO <sub>3</sub>	140	Penta	200
1k	KTi	27	Co(Ac) <sub>2</sub>	127	100	PO <sub>3</sub>	121	-	-
1l	Sb <sub>2</sub> O <sub>3</sub>	390	-	-	-	PO <sub>3</sub>	-	-	-

[表 2]

[Table 2]

表 2

実施例 番号	溶融融合		SV	[COOH] (mmol/kg)	DBG (%)	色数			固相重合		SV
	圧力	時間				L*	a*	b*	時間	温度	
	(mbar)	(分)							(時)	(℃)	
1b	1.1	-	0.851	11	0.47	65.76	-1.19	5.89	14	220	1.048
1c	0.9	-	0.835	15	0.48	66.57	-0.62	4.07	16	220	1.057
1d	0.8	-	0.835	13	0.48	64.95	0.12	0.98	18.5	220	1.019
1e	1.1	-	0.826	10	0.53	67.30	0.12	0.77	14	220	1.032
1f	1.6	-	0.848	12	0.55	66.19	-0.94	4.92	10.5	220	1.063
1g	1.0	-	0.840	12	0.50	64.37	0.27	-0.11	16	220	1.000
1h	1.3	-	0.846	17	0.53	66.28	-0.03	2.34	14	220	1.055
1i	1.6	-	0.829	13	0.55	64.07	-2.31	7.27	9.25	220	1.038
1j	0.8	141	0.832	15	0.74	62.75	0.86	2.65	12	225	1.048
1k	0.8	189	0.853	9	0.72	66.35	-0.30	-0.19	12	220	1.134
1l	0.8	184	0.834	11	0.63	64.64	-2.51	4.16	12	225	1.053

実施例 2

Working Example 2

以下の実施例は、直接エステル化によるポリエステル製造を示す。

## 【0058】

エステル化反応器に、テレフタル酸 8.29kg、イソフタル酸 0.124kg、およびエチレングリコール 4.0kg を充填し、攪拌および不活性ガスとしての窒素下、混合物を、圧力 3.2 バール下、除去される水が留去されるように加熱する。

水の除去が終了した時、溶融反応生成物を重縮合容器に移し、錯形成剤としての  $H_3PO_3$  0.35g (32ppm) および酢酸コバルト・4 水和物 1.47g (135ppm) (Co 32ppm に相当) を加えた。

しかる後、カリウムチタニルオキサレート 0.49g (45ppm) (Ti 6.1ppm に相当) を加え、このバッチを窒素下 240 deg C で攪拌し、幾分減圧にしてエチレングリコールを留去する。

ついで、1時間の間に、初期圧を 1.13 ミリバールに低下させ、その間、溶融物の温度は、240 deg C から 270 deg C に上昇する。

ついで、さらに 30 分の間に、温度を 280 deg C に上昇させ、溶融物の試料が、溶融物 1g のジクロロ酢酸 100ml 溶液中 25 deg C で測定して、比溶液粘度 0.83 になるまで、攪拌を継続する。

## 【0059】

溶融物は、冷却し、慣用的な方法で加工して、径 2~3mm を有するペレットとする。

かくして得られたポリエステルは、以下の特性値:

カルボキシル基含量 [mmol/kg]: 13				
carboxyl group content [mmol/kg]: 13				
ジエチレングリコールの含量 [%]				9
content of diethylene glycol [%]				9

1.5

を有する。

## 【0060】

かくして、製造されたポリエステルは、固相縮合によって、さらに縮合することができる。

このために、上記製造したペレットは、緩やかに全体を混合しながら、窒素下または減圧下、220

Working Example below shows production of polyester with direct esterification.

## 【0058】

In esterification reactor, terephthalic acid 8.29 kg, isophthalic acid 0.124 kg, and ethyleneglycol 4.0 kg it is filled, in order under the nitrogen as agitation and inert gas, blend, under pressure 3.2 bar, for the water which is removed to be removed, it heats.

When removal of water ends, melt reaction product was moved to the condensation polymerization container,  $H_3PO_3$  0.35g as complexing agent (32 ppm) and cobalt acetate \* tetrahydrate 1.47g (135 ppm) (Suitable to Co 32 ppm) was added.

After that, this batch is agitated with 240 deg C under nitrogen including potassium titanyl oxalate 0.49g (45 ppm) (Suitable to Ti 6.1 ppm), ethyleneglycol is removed somewhat to vacuum.

Next, between 1 hour, initial pressure decreasing to 1.13 millibar, at that time, temperature of melt from 240 deg C rises in 270 deg C.

Next, furthermore between 30 min, temperature rising in 280 deg C, the sample of melt, with 25 deg C in dichloroacetic acid 100 ml solution of melt 1g measuring, until it becomes ratio solution viscosity 0.83, it continues agitation.

## 【0059】

It cools melt, processes with usual method, it makes pellet which possesses diameter 2 - 3 mm.

As for polyester which it acquires in this way, property value: below

1.5

It possesses.

## 【0060】

This way, with solid phase condensation, furthermore it can condense the polyester which is produced.

Because of this, description above while mixing entirety leniently, under nitrogen or under vacuum, 9.5 hours it heats

deg C で9.5 時間加熱する。

上記のように測定した比粘度 1.087 を有するポリエステルが、かくして、得られる。

[0061]

さらに、ポリエステルは、表 3 および表 4 から理解できるような条件下、類似した方法で製造することができる。

生成物は、表 4 に見られるような特徴を有する。

[0062]

[表 3]

pellet which is produced, with 220 deg C.

As description above polyester which possesses specific viscosity 1.087 which was measured, is acquired this way.

[0061]

Furthermore, under condition which you can understand from Table 3 and Table 4, it can produce polyester, with method which resembles.

As for product, it possesses kind of feature which is seen in Table 4.

[0062]

[Table 3]

表 3

実施例 番号	重縮合触媒		コバルト化合物			錯形成剤		添加剤	
	性質	量 (ppm)	性質	量 (ppm)	(%) 遊離	性質	量 (ppm)	性質	量 (ppm)
2b	Sb <sub>2</sub> O <sub>3</sub>	298	-	-	-	H <sub>3</sub> PO <sub>3</sub>	32	Penta	200
2c	KTi	45	Co(Ac) <sub>2</sub>	84	100	-	-	Penta	200
2d	KTi	45	Co(Ac) <sub>2</sub>	135	25	H <sub>3</sub> PO <sub>3</sub>	32	Penta	200

[表 4]

[Table 4]

表 4

実施例 番号	溶融融合 圧力 (mbar)	SV	[COOH] (mmol/kg)	DEG (%)	色数		
					L*	a*	b*
2b	2.75	0.812	20	1.51	62.8	-1.8	5.2
2c	4.7	0.814	21	1.49	63.6	0.5	4.7
2d	2.35	0.823	12	1.36	64.6	1.7	0.9

## 【図面の簡単な説明】

## 【図1】

錯形成剤対コバルト化合物の比に対してプロットした粘度を表わす予備実験の結果を示すグラフである。

## Drawings

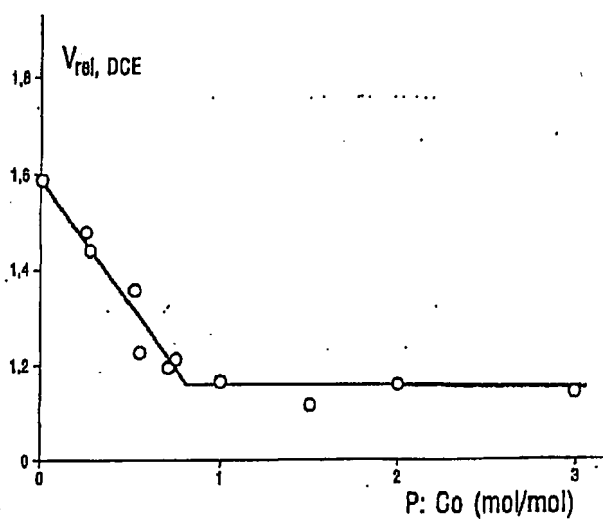
## 【図1】

## [Brief Explanation of the Drawing(s)]

## [Figure 1]

It is a graph which shows result of preparatory experiment which displays the viscosity which plot is done vis-a-vis ratio of complexing agent anti-cobalt compound.

## [Figure 1]





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## Abstract

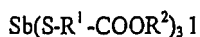
(57)【要約】

【目的】

延伸成形用ボトル、フィルムなどに好適な曇りがなく透明なポリエステルを製造する方法を提供する。

【構成】

ジカルボン酸成分とグリコールとからポリエステルの製造するに際し、下記式 1 で表わされるアンチモン化合物を重縮合触媒として使用する。



(R<sup>1</sup> は炭素数 1~10 の 2 価の有機基を示し、R<sup>2</sup> は炭素数 1~10 の 1 価の有機基を示す。)

## Claims

【特許請求の範囲】

(57) [Abstract]

[Objective]

There is not a preferred haze in bottle, film etc for drawing and molding and it offers the method which produces transparent polyester.

[Constitution]

When polyester is produced from dicarboxylic acid component and glycol, you use antimony compound which is displayed with below-mentioned Formula 1 as the condensation catalyst.

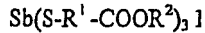


(R<sup>1</sup> shows organic group of divalent of carbon number 1~10, R<sup>2</sup> shows organic group of univalent of carbon number 1~10.)

[Claim(s)]

## 【請求項 1】

ジカルボン酸成分とグリコールとからポリエステルを製造するに際し、下記式 1 で表わされるアンチモン化合物を重縮合触媒として使用することを特徴とするポリエステルの製造方法。



( $\text{R}^1$  は炭素数 1~10 の 2 価の有機基を示し、 $\text{R}^2$  は炭素数 1~10 の 1 価の有機基を示す。)

## Specification

## 【発明の詳細な説明】

## 【0001】

## 【産業上の利用分野】

本発明は、延伸成形用ボトル、フィルムなどの製造に好適な曇りがなく透明なポリエステルの製造する方法に関するものである。

## 【0002】

## 【従来の技術】

ポリエチレンテレフタレート(PET)は機械的強度、化学的安定性、透明性などに優れており、各種のシート、フィルム、容器などとして幅広く用いられている。

そして、PET は、工業的にはテレフタル酸又はジメチルテレフタレートとエチレングリコールとからエステル化もしくはエステル交換によりビス( $\beta$ -ヒドロキシエチル)テレフタレート(その低重合体を含む)を得、これを高温、高減圧下に重縮合する方法により製造されている。

## 【0003】

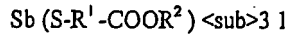
PET を製造する際の重縮合反応の触媒としては、アンチモン化合物、特に三酸化アンチモンが安価でかつ触媒活性が優れているため最も広く用いられている。

しかしながら、アンチモン化合物を重縮合触媒として用いると、得られるポリマーが黒ずんだ灰色の色調となり、フィルムとして使用したときには透明性が低下し、繊維として使用したときには白度が低下したり、染色物の鮮明さに欠けたりするなど、製品の品質を低下させる。

特にアンチモン化合物の使用量を増加した場合にはこの黒ずみ現象が著しくなるので、触媒量を抑えねばならないという問題点があった。

## [Claim 1]

When polyester is produced from dicarboxylic acid component and glycol, you use antimony compound which is displayed with below-mentioned Formula 1 as the condensation catalyst manufacturing method. of polyester which is made feature



( $\text{R}^1$  shows organic group of divalent of carbon number 1~10,  $\text{R}^2$  shows organic group of univalent of carbon number 1~10.)

## [Description of the Invention]

## [0001]

## [Field of Industrial Application]

this invention is not a preferred haze in bottle, film or other production for drawing and molding and it is something regarding method which produces transparent polyester.

## [0002]

## [Prior Art]

polyethylene terephthalate (PET) is superior in mechanical strength, chemical stability, transparency, etc widely is used as various sheet, film, container etc.

And, PET from terephthalic acid or dimethyl terephthalate and ethyleneglycol with the esterification, or ester exchange obtains bis ( $\beta$ -hydroxyethyl) terephthalate (low molecular weight polymer is included.) in industrially is produced this by method which condensation polymerization is done under high temperature, highly reduced pressure.

## [0003]

When producing PET, antimony compound, especially antimony trioxide being inexpensive as catalyst of condensation polymerization, and because catalytic activity is superior, it is most widely used.

But, when antimony compound when it uses, as condensation catalyst it becomes color of ash color where polymer which is acquired blackens, when using, as film transparency decreases, using as fiber, whiteness decreases, becomes insufficient such as, quality of product decreases in vividness of dyed article.

Especially when amount used of antimony compound it increases, because this mildew phenomena becomes considerable, catalyst amount must be held down, there was a problem.

[0004]

アンチモン化合物に基づくポリマーのくすみを解消するには、基本的には重縮合系内におけるアンチモン化合物の還元電位が三酸化アンチモンを用いた場合に比べて高くなるようなアンチモン化合物、すなわち、重縮合系中で還元され難いアンチモン化合物を使用すればよい。

[0005]

このような背景から、ポリマーにくすみを生じないアンチモン化合物系触媒が種々提案されている。

例えば、特公昭 36- 10847 号公報及び同 39-6397 号公報には  $Sb_2O_5$  のような五価のアンチモン化合物が、特公昭 43- 15999 号公報には  $(C_6H_5)_3SbO$  又は  $(CH_3)_3Sb(OH)_2$  のような五価の有機アンチモン化合物が、特公昭 46-3998 号公報には  $C_{12}$  以上の脂肪族カルボン酸のアンチモン塩が、そして、特公昭 53-1320 号公報には  $\alpha$ -オキシカルボン酸又は  $\alpha$ 、 $\beta$ -ジカルボン酸の酸素原子のうち、少なくとも 1 つを硫黄で置換した化合物の環状アンチモン塩などが示されている。

これらのアンチモン化合物は、いずれもポリマーのくすみを低減化させるのには有効であるが、 $Sb_2O_5$  のような五価のアンチモン化合物は三酸化アンチモンに比べてコストが高い。

また、 $C_{12}$  以上の脂肪族カルボン酸のアンチモン塩は、くすみの低減効果が五価のアンチモン化合物に比べて不十分である上、重縮合速度が遅いので、三酸化アンチモンに比べて大量に使用する必要があり、工業的な触媒としては満足すべきものではない。

また、環状のアンチモン塩は重縮合の際開環し、これがポリマーと反応して末端基を封鎖するため、重縮合速度が低下するという問題があった。

[0006]

【発明が解決しようとする課題】

本発明は、重縮合触媒としてアンチモン化合物を使用して、くすみがなく透明性に優れたポリエステルを製造する方法を提供しようとするものである。

[0007]

[0004]

dullness of color of polymer which is based on antimony compound is cancelled, in basic when reduction potential of antimony compound in condensation polymerization inside of system uses antimony trioxide comparing, if you should have used antimony compound which is difficult to be reduced in antimony compound, namely, condensation polymerization kind of system which becomes high.

[0005]

From this kind of background, antimony compound -based catalyst which does not cause dullness of color in polymer is proposed various.

In for example Japan Examined Patent Publication Sho 36- 10847 disclosure and same 39 - 6397 disclosure antimony compound of pentavalent like  $Sb_2O_5$ , in Japan Examined Patent Publication Sho 43- 15999 disclosure  $(C_6H_5)_3SbO$  or  $(CH_3)_3Sb(OH)_2$  organic antimony compound of the pentavalent way, in Japan Examined Patent Publication Sho 46-3998 disclosure antimony salt of aliphatic carboxylic acid above the  $C_{12}$ , and, in Japan Examined Patent Publication Sho 53- 1320 disclosure the  $\alpha$ -hydroxy carboxylic acid or the  $\alpha$  and the  $\beta$ -dicarboxylic acid among oxygen atom, annular antimony salt etc of compound which substitutes at least one with sulfur is shown.

These antimony compound, in each case in order reduction to do dullness of color of the polymer, are effective, but as for antimony compound of pentavalent like  $Sb_2O_5$  cost is high in comparison with antimony trioxide.

In addition, because as for antimony salt of aliphatic carboxylic acid above  $C_{12}$ , reducing effect of dullness of color in addition to being a unsatisfactory in comparison with antimony compound of pentavalent, condensation polymerization velocity is slow, it is necessary to use for large scale in comparison with antimony trioxide, as industrial catalyst it is not something which it should be satisfied.

In addition, case of condensation polymerization ring opening it does antimony salt of the annular, this reacts with polymer and in order capped chain to do the end group, there was a problem that condensation polymerization velocity decreases.

[0006]

[Problems to be Solved by the Invention]

It is something which this invention using antimony compound as condensation catalyst, tries will not be a dullness of color and to offer method which produces polyester which is superior in transparency.

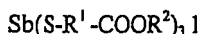
[0007]

## 【課題を解決するための手段】

本発明者らは、上記の課題を解決するために鋭意検討した結果、特定のアンチモン化合物を重縮合触媒として使用することにより、くすみがなく透明性に優れたポリエステルを得ることができるとを見出し、本発明に到達した。

【0008】

すなわち、本発明の要旨は、ジカルボン酸成分とグリコールとからポリエステルを製造するに際し、下記式1で表わされるアンチモン化合物を重縮合触媒として使用することを特徴とするポリエステルの製造方法にある。



( $\text{R}^1$  は炭素数 1~10 の 2 価の有機基を示し、 $\text{R}^2$  は炭素数 1~10 の 1 価の有機基を示す。)

【0009】

以下、本発明について詳細に説明する。

【0010】

本発明で使用するジカルボン酸成分としては、テレフタル酸又はテレフタル酸ジメチルが好ましく用いられる。

これらを主体とし、イソフタル酸、無水フタル酸、2,6-ナフタレンジカルボン酸、5-ナトリウムスルホイソフタル酸、アジピン酸、コハク酸等のジカルボン酸及びそれらの低級アルキルエステルやp-ヒドロキシ安息香酸などのヒドロキシカルボン酸を共重合体成分として併用してもよい。

【0011】

本発明で使用するグリコールとしては、エチレングリコール、1, 4-ブタンジオール、1, 3-プロパンジオール、1, 6-ヘキサジオール及び1, 4-シクロヘキサジメタノールが好ましく用いられる。

これらを主体とし、ジエチレングリコール、ポリエチレングリコール、ネオペンチルグリコール、ビスフェノール A のエチレンオキシド付加物、ビスフェノール S のエチレンオキシド付加物、キシリレングリコールなど共重合体成分として併用してもよい。

【0012】

また、重縮合時に、エステル化反応あるいはエステル交換反応時に添加した触媒やリン化合物のような安定剤、滑剤、酸化防止剤等の添加剤が共存していても差し支えない。

## [Means to Solve the Problems]

these inventors is not a dullness of color in order to solve above-mentioned problem result of diligent investigation, specific antimony compound as condensation catalyst by using, can acquire polyester which is superior in transparency to discover, it arrived in this invention.

【0008】

As for gist of namely, this invention, when polyester is produced from the dicarboxylic acid component and glycol, antimony compound which is displayed with the below-mentioned Formula 1 you use as condensation catalyst there is a manufacturing method of the polyester which is made feature.



( $\text{R}^1$  shows organic group of divalent of carbon number 1~10,  $\text{R}^2$  shows organic group of univalent of carbon number 1~10.)

【0009】

You explain in detail below, concerning this invention.

【0010】

It can use terephthalic acid or dimethyl terephthalate desirably as dicarboxylic acid component which is used with this invention.

It designates these as main component, it is possible to jointly use the isophthalic acid, phthalic anhydride, 2,6-naphthalenedicarboxylic acid, 5-sodium sulfo isophthalic acid, adipic acid, succinic acid or other dicarboxylic acid and those lower alkyl ester and p-hydroxybenzoic acid or other hydroxycarboxylic acid as copolymer component.

【0011】

It can use ethyleneglycol, 1, 4-butanediol, 1, 3-propanediol, 1, 6-hexanediol and 1 and 4-cyclohexanediol desirably as glycol which is used with this invention.

It designates these as main component, it is possible to jointly use as copolymer component such as diethylene glycol and ethylene oxide adduct, xylylene glycol of ethylene oxide adduct, bisphenol S of polyethylene glycol, neopentyl glycol, bisphenol A.

【0012】

In addition, at time of condensation polymerization, stabilizer, lubricant, antioxidant or other additive like catalyst and phosphorus compound which are added at time of esterification reaction or ester exchange reaction having associated it does not become inconvenient.

【0013】

一般的に共重合成分を添加すると重縮合反応速度が遅くなるが、本発明の方法によると、アンチモン化合物の添加量を増やしてもポリマーにくすみが生じないので、アンチモン化合物の添加量を増やして反応速度を上げることができ、共重合ポリエステルも生産性良く製造することができる。

【0014】

本発明の方法は、通常の PET の製造方法に準じて実施することができ、例えば、テレフタル酸とエチレングリコールとをエステル化反応させ、次いで反応生成物を重縮合させて所定の極限粘度のポリエステルとする方法で行うことができる。

エステル化反応は 245~260 deg C の温度で行うのが好ましく、重縮合反応は 5hPa 以下の高真空で、ポリエステルの融点~300 deg C の温度で行うのが好ましい。

重縮合温度が 300 deg C を超えるとポリマーの色相が悪化するので好ましくない。

【0015】

本発明で使用するアンチモン化合物は、アンチモン原子がメルカプトカルボン酸中の硫黄原子と結合していることが必要である。

このアンチモン化合物の具体的な例としては次のようなものを挙げることができる。

【0016】

【化 1】

coexisted, it does not become inconvenient.

【0013】

When copolymer component is added generally, condensation polymerization speed becomes slow but, with method of this invention, increasing addition quantity of antimony compound, because the dullness of color does not occur in polymer, increasing addition quantity of antimony compound, it increases reaction rate, it is possible, productivity can produce also copolyester well.

【0014】

Executes method of this invention, according to manufacturing method of conventional PET to be possible, esterification reaction doing for example terephthalic acid and ethyleneglycol, condensation polymerization doing the reaction product next, it does with method which it makes polyester of the predetermined intrinsic viscosity it is possible.

As for esterification reaction it is desirable to do with temperature of 245 - 260 deg C, condensation polymerization with high vacuum of 5 hPa or less, doing with temperature of melting point~300 deg C of polyester is desirable.

When condensation polymerization temperature exceeds 300 deg C, because hue of polymer deteriorates, it is not desirable.

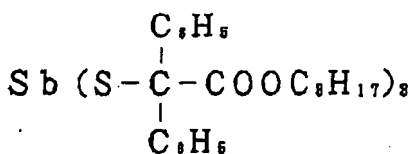
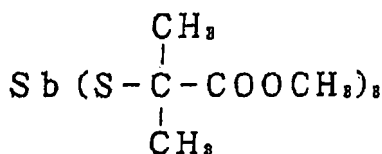
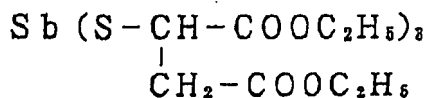
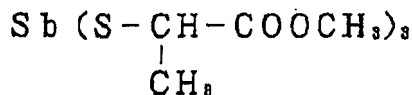
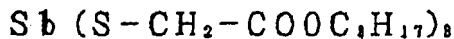
【0015】

antimony atom has connected antimony compound which is used with this invention, with sulfur atom in mercapto carboxylic acid, it is necessary.

Next kind of ones can be listed as concrete example of this antimony compound.

【0016】

[Chemical Formula 1]



[0017]

上記のようなアンチモン化合物は、ポリエステル  
の重合反応系内に容易に溶解するが、水には  
不溶であり、室温ではほとんど加水分解を受け  
ない。

また、これらのアンチモン化合物の中には常温  
で液体で、反応容器に投入する際にグリコール  
などに溶解させる必要がないものもある。

[0018]

また、アンチモン化合物は重縮合反応初期まで  
の任意の時期に添加できるが、重縮合反応直  
前に添加することが好ましい。

[0017]

As description above it melts antimony compound, easily  
inside polymerization reaction system of polyester, but with  
insoluble, with room temperature hydrolysis is not received to  
water for most part.

In addition, when in these antimony compound with liquid,  
throwing to reactor with ambient temperature, there are also  
some which do not have necessity to melt in glycol etc.

[0018]

In addition, it can add antimony compound to time of option  
to condensation polymerization first stage, but, it adds  
immediately before condensation polymerization it  
is desirable.

[0019]

本発明において、アンチモン化合物は、通常、原料の酸成分1モルに対するアンチモン原子のモル数として、 $4 \times 10^{-5}$ ~ $4 \times 10^{-3}$ モルの範囲で使用される。

アンチモン化合物の使用量が  $4 \times 10^{-5}$  モルより少ないと、重縮合反応を行うに十分な触媒活性が得られない。

また、 $4 \times 10^{-3}$  モルより多く用いても、効果が飽和してしまうので、実用上意味がない。

[0020]

また、他の重縮合触媒、例えば酸化ゲルマニウム、テトラブチルチタネートなどを本発明の効果を損なわない範囲で併用してもよい。

[0021]

【作用】

本発明の方法によると、重縮合触媒としてアンチモン化合物を用いているにもかかわらず、得られるポリマーは優れた透明性を示す。

これは、本発明で使用するアンチモン化合物は、ポリエステル中への溶解性が高いとともに、三酸化アンチモンよりも還元されにくい化合物であるので、重縮合過程において、くすみの原因となる金属アンチモンの析出が少ないためと認められる。

[0022]

【実施例】

次に、実施例をあげて本発明を具体的に説明する。

なお、実施例においてポリエステルの特性値は次のようにして測定した。

(a) 熔融ポリマーの透明性

ランダムに選出した5人のパネラーによって、肉眼によりくすみの有無を1~5の5段階で判定し、その合計点によって次の3段階で評価した。

[0019]

Regarding to this invention, antimony compound is used in range of  $4 \times 10^{-5}$ ~ $4 \times 10^{-3}$  mole usually, as number of moles of antimony atom for acid component 1 mole of starting material.

When amount used of antimony compound is less than  $4 \times 10^{-5}$  mole, does condensation polymerization the sufficient catalytic activity is not acquired.

In addition, using more than  $4 \times 10^{-3}$  mole, because effect is saturated, there is not meaning in regard to utility.

[0020]

In addition, it is possible to jointly use other condensation catalyst, for example germanium oxide, tetrabutyl titanate etc in the range which does not impair effect of this invention.

[0021]

[Working Principle]

As condensation catalyst has used antimony compound of polymer which is acquired inspite, shows transparency which is superior with method of this invention.

As for this, as for antimony compound which is used with this invention, solubility to in polyester is high because it is a compound which is difficult to be reduced and also, in comparison with antimony trioxide, for sake of precipitation of metal antimony which becomes cause of dullness of color in the condensation polymerization process, is little it is recognized.

[0022]

[Working Example(s)]

Next, listing execution example, you explain this invention concretely.

property value of polyester measured furthermore, in Working Example the following way.

transparency of (a) molten polymer

With panel member of 5 persons which are elected in random, it decided presence or absence of dullness of color with 5 steps 1 - 5 with naked eye, with the point total evaluation did with next 3 stages.

○(良好)		:20 以上			
○(Satisfactory)		: 20 or greater			
△(やや良好):15 以上 20 未満					



* (A little satisfactory): Under of 15 or greater 20					
× (不良)		: 15 未満			
X (deficiency)		: 15 under			
(b) プレート		—ズ			
(b) plate		—ズ			

プレートに射出成形して(成形温度 285 deg C)、プレートの透明度を日本電色工業社製の濁度計 MODEL 1001DP で評価した(空気:ヘーズ 0%)。

(プレートヘーズの値が小さい程透明であり、10 未満を合格とした。)

(c) 極限粘度[ $\eta$ ]

フェノールと四塩化エタンとの等重量混合物を溶媒として、温度 20.0 deg C で測定した。

(d) 色調

日本電色工業社製の色差計 ND  $\Sigma$  80 型を用いて測定した。

色調の判定は、ハンターの Lab 表色計で行った。

L 値は明度(値が大きい程明るい)、a 値は赤-緑系の色相(+は赤味、-は緑味)、b 値は黄-青系の色相(+は黄味、-は青味)を表わす。

ポリマーの色調としては L 値が大きいほど、a 値が 0 に近いほど、また極端に小さくならない限り b 値が小さいほど良好である。

【0023】

実施例 1

ビス( $\beta$ -ヒドロキシエチル)テレフタレート(BHET)及びその低重合体の存在するエステル化反応缶に、テレフタル酸(TPA)とエチレングリコール(EG)とのモル比 1/1.6 のスラリーを連続的に供給し、温度 250 deg C、圧力 49hPaG、滞留時間 8 時間の条件で反応させ、平均重合度 7 のエステル化生成物を連続的に得た。

このエステル化生成物 60kg を反応器に仕込み、触媒として酸成分 1 モルに対するアンチモン原子のモル数として  $4 \times 10^{-4}$  モルのアンチモントリス(オクチルチオグリコラート)を加え、温度

injection molding doing in plate, (molding temperature 285 deg C), evaluation it did clarity of the plate with turbidity meter model 1001DP of Nippon Denshoku Kogyo K.K. (DB 69-244-3708 ) supplied, (air: haze 0% ).

(When value of plate haze is small, with transparent , it made under 10passing. )

(c) intrinsic viscosity [ $\eta$ ]

With equal weight blend of phenol and tetrachloroethane as solvent, it measured with temperature 20.0 deg C.

(d) color

It measured making use of color difference meter ND Model :si 80 of Nippon Denshoku Kogyo K.K. (DB 69-244-3708 ) supplied.

It decided color, with Labsurface color meter of Hunter.

As for L value lightness (Extent whose value is large it is bright. ), as for a value red -green hue of system (As for + as for redness, - greenishness ), as for b value hue (As for + as for yellowing, - blueness ) of yellow-blue type is displayed.

When L value is large as color of polymer, if extent where a value is close to 0, in addition it does not become extremelysmall when b value is small, it is satisfactory.

【0023】

Working Example 1

bis ( $\beta$ -hydroxyethyl ) terephthalate (BHET ) and in esterification reaction can where its low molecular weight polymer exists, the terephthalic acid (TPA ) with ethyleneglycol (EG ) with it supplied slurry of mole ratio 1/1.6 to continuous, reacted with condition of temperature 250 deg C, pressure 49 hPaG, residence time 8-hour, acquired esterification product of average degree of polymerization 7 in continuous.

This esterification product 60 kg was inserted in reactor , 2 hours condensation polymerization were done with temperature 280 deg C, pressure 0.9 hPa including antimony tris (octyl thio glycolate ) of  $4 \times 10^{-4}$  mole as number of moles

280 deg C、圧力 0.9hPa で 2 時間重縮合反応を行った。

得られたポリマーは溶融時の透明性が良好で、黒ずんだくすみは認められなかった。

また、極限粘度 0.76dl/g、L 値 69.0、a 値+0.5、b 値+7.0、プレートヘイズ 2.4%であった。

【0024】

実施例 2~7 及び比較例 1~3

アンチモン化合物の種類及びその添加量を変えた以外は、実施例 1 と同様にしてポリエステルを製造した。

得られたポリマーの特性値を表 1 に示す。

【0025】

実施例 8

TPA 26.6kg、BHET 8.0kg、1, 4-シクロヘキサンジメタノール 23.1kg、EG 2.5kg 及びビスフェノール S のエチレンオキシド付加物 6.8kg をエステル化反応缶に仕込み、温度 260 deg C で 4 時間エステル化反応を行い、重縮合反応器に送液した後、触媒として酸成分 1 モルに対するアンチモン原子のモル数として  $4 \times 10^{-4}$  モルのアンチモントリス(オクチルチオグリコラート)を加え、温度 280 deg C、圧力 0.9hPa で 3 時間重縮合反応を行った。

得られたポリマーの特性値を表 1 に示す。

【0026】

【表 1】

of antimony atom for the acid component 1 mole as catalyst.

As for polymer which it acquires transparency when melting beingsatisfactory, as for dullness of color which blackens it was not recognized.

In addition, intrinsic viscosity 0.76 dl/g、L value 69.0、a value+0.5、b value + 7.0, it was a plate haze 2.4%.

【0024】

Working Example 2~7 and Comparative Example 1~3

types of antimony compound and other than changing its addition quantity, polyester was produced to similar to Working Example 1.

property value of polymer which it acquires is shown in Table 1.

【0025】

Working Example 8

ethylene oxide adduct 6.8 kg of TPA 26.6 kg、BHET 8.0 kg、1, 4- cyclohexane dimethanol 23.1 kg、EG 2.5 kg and bisphenol S was inserted in esterification reaction can, 4 hours esterification reaction were done with temperature 260 deg C, 3 hours condensation polymerization were done with temperature 280 deg C、pressure 0.9 hPa including antimony tris (octyl thio glycolate ) of  $4 \times 10^{-4}$  mole as number of moles of antimony atom for the acid component 1 mole liquid transport after doing, as catalyst in polycondensation reactor.

property value of polymer which it acquires is shown in Table 1.

【0026】

[Table 1]

		重縮合触媒		〔η〕 (dl/g)	溶融 ポリマー 透明性	色調			プレート ヘーズ (%)
		アンチモン化合物	添加量			L値	a値	b値	
実施例	1	$\text{Sb}(\text{S}-\text{CH}_2-\text{COOC}_6\text{H}_{17})_3$	4.0	0.76	○	69.0	+0.5	+7.0	2.4
	2	$\text{Sb}(\text{S}-\text{CH}_2-\text{COOC}_6\text{H}_{17})_3$	2.0	0.70	○	68.3	+0.3	+6.2	4.3
	3	$\text{Sb}(\text{S}-\text{CH}_2-\text{COOC}_6\text{H}_{17})_3$	8.0	0.81	○	68.8	+0.6	+7.5	1.9
	4	$\begin{array}{c} \text{Sb}(\text{S}-\text{CH}-\text{COOCH}_3)_3 \\   \\ \text{CH}_3 \end{array}$	4.0	0.77	○	68.9	+0.7	+7.1	3.3
	5	$\begin{array}{c} \text{CH}_3 \\   \\ \text{Sb}(\text{S}-\text{C}-\text{COOCH}_3)_3 \\   \\ \text{CH}_3 \end{array}$	4.0	0.74	○	67.5	+0.1	+6.5	5.9
	6	$\begin{array}{c} \text{Sb}(\text{S}-\text{CH}-\text{COOC}_2\text{H}_5)_3 \\   \\ \text{COOC}_2\text{H}_5 \end{array}$	4.0	0.74	○	69.2	+0.4	+6.6	2.7
	7	$\text{Sb}(\text{S}-\text{C}_8\text{H}_4-\text{COOC}_6\text{H}_{17})_3$	4.0	0.73	○	66.3	+0.4	+5.8	7.6
	8	$\text{Sb}(\text{S}-\text{CH}_2-\text{COOC}_6\text{H}_{17})_3$	4.0	0.80	○	68.3	-0.3	+4.9	4.7
比較例	1	$\text{Sb}_2\text{O}_3$	2.0	0.74	△	58.3	-0.3	+5.2	19.7
	2	$\text{Sb}_2\text{O}_3$	4.0	0.80	×	55.2	+0.1	+6.0	23.5
	3	$(\text{CH}_3\text{COO})_3\text{Sb}$	4.0	0.75	×	55.4	-0.4	+8.2	23.4

注：添加量の単位は、 $10^{-4}$ モル/酸成分モル

【0027】

【発明の効果】

本発明によれば、優れた透明性を有するポリエステルを製造することが可能となる。

また、重縮合過程でアンチモン化合物が金属アンチモンに還元される量が少なくなり、実質上のアンチモン化合物濃度が高くなるため、生産性が大きく向上する。

さらに、ポリマーのくすみがないため、触媒使用量を多くすることも可能で、生産性を飛躍的に向上でき、操作性も良好で、得られるポリマーは、透明性が必要とされる成形品やフィルム用として好適に使用される。

[0027]

[Effects of the Invention]

According to this invention, polyester which possesses transparency which is superior is produced becomes possible.

In addition, quantity where antimony compound is reduced to metal antimony with condensation polymerization process decreases, because antimony compound concentration with respect to substance becomes high, productivity improves largely.

Furthermore, because there is not a dullness of color of polymer, also being possible to make amount of catalyst used many, productivity be able to improve rapidly, also operation is satisfactory, polymer which is acquired is used for ideal as molded article and one for film where transparency is needed.

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Abstract

(57)【要約】

(57) [Abstract]

【課題】

[Problems to be Solved by the Invention]

二軸延伸フィルムや繊維に成型した場合、優れた耐摩耗性を示し、特に磁気テープの支持体に用いた場合、優れた耐摩耗性、耐久性を示すポ

When molding it does in biaxially drawn film and fiber, abrasion resistance which is superior is shown, when it uses for support of especially magnetic tape, polyester composition

リエステル組成物を得る。

【解決手段】

結晶構造の異なる二種類以上の酸化アルミニウム粒子を併用し、リン化合物およびアンモニア又は低級アミン化合物を添加して湿式分散処理してポリエステル中に良好に分散し、耐摩耗性に優れたフィルムあるいは繊維およびその他の成形品を得るに適したポリエステル組成物を得る。

Claims

【特許請求の範囲】

【請求項 1】

芳香族ジカルボン酸を主たる酸成分とし、脂肪族グリコールを主たるグリコール成分とするポリエステルを製造するに際し、重合反応の完結するまでの任意の時点で結晶構造の異なる少なくとも二種類以上の酸化アルミニウム粒子を溶媒の存在下、リン化合物およびアンモニア又は低級アミン化合物を添加して湿式分散処理したスラリーを添加することを特徴とするポリエステル組成物の製造方法。

【請求項 2】

酸化アルミニウム粒子が $\alpha$ 型、 $\gamma$ 型、 $\delta$ 型、および $\theta$ 型よりなる群から選ばれた二種以上であることを特徴とする請求項 1 記載のポリエステル組成物の製造方法。

【請求項 3】

酸化アルミニウム粒子が $\delta$ 型および $\theta$ 型から選ばれた二種以上であることを特徴とする請求項 2 記載のポリエステル組成物の製造方法。

【請求項 4】

酸化アルミニウム粒子の B.E.T.法による比表面積が  $50\sim 300\text{m}^2/\text{g}$  であることを特徴とする請求項 1~3 のいずれかに記載のポリエステル組成物の製造方法。

【請求項 5】

酸化アルミニウム粒子の B.E.T.法による全細孔容積が  $0.2\sim 1.5\text{ml/g}$  であることを特徴とする請求項 1~4 のいずれかに記載のポリエステル組成物の製造方法。

【請求項 6】

which shows abrasion resistance, durability which is superior is obtained.

【Means to Solve the Problems】

Jointly using aluminum oxide particle of two kinds or more where crystal structure differs, adding phosphorus compound and ammonia or lower amine compound and wet type dispersing doing it disperses in polyester satisfactorily, film or fiber and other molded article which are superior in abrasion resistance it is obtained it obtains the polyester composition which is suited.

【Claim(s)】

【Claim 1】

aromatic dicarboxylic acid is designated as main acid component, when polyester which designates aliphatic glycol as main glycol component is produced, until polymerization reaction it completes, aluminum oxide particle above at least two kinds where crystal structure differs in the time point of option under existing of solvent, Adding phosphorus compound and ammonia or lower amine compound, it adds slurry which wet type dispersing is done manufacturing method. of polyester composition which is made feature

【Claim 2】

aluminum oxide particle the;  $\alpha$ -type, the;  $\gamma$ -type, is 2 kinds or more which are chosen from group which consists of the;  $\delta$ -type, and the;  $\theta$  type and the manufacturing method. of polyester composition which is stated in Claim 1 which is made feature

【Claim 3】

aluminum oxide particle is 2 kinds or more which are chosen from the;  $\delta$ -type and the;  $\theta$  type and manufacturing method. of polyester composition which is stated in Claim 2 which is made feature

【Claim 4】

specific surface area is  $50 - 300\text{m}^2/\text{g}$  with BET method of aluminum oxide particle and manufacturing method. of polyester composition which is stated in any of Claim 1~3 which is made feature

【Claim 5】

total pore volume is  $0.2 - 1.5\text{ml/g}$  with BET method of aluminum oxide particle and manufacturing method. of polyester composition which is stated in any of Claim 1~4 which is made feature

【Claim 6】

酸化アルミニウム粒子の水銀およびヘリウム置換法による空隙率が 60%以上であることを特徴とする請求項 1~5 のいずれかに記載のポリエステル組成物の製造方法。

【請求項 7】

リン化合物およびアンモニア又は低級アミン化合物がスラリー中で第 4 級アンモニウム—リン酸塩または、第 3 級アミン—リン酸塩を形成していることを特徴とする請求項 1~6 のいずれかに記載のポリエステル組成物の製造方法。

Specification

【発明の詳細な説明】

【0001】

【発明の属する技術分野】

本発明は、ポリエステル組成物の製造方法に関するものであり、さらに詳しくは酸化アルミニウム粒子を特定の条件下でよく分散させ、ポリエステル中に良好に分散した状態で配合し、耐摩耗性に優れたフィルムあるいは繊維を得るに適したポリエステル組成物を製造する方法に関する。

【0002】

【従来の技術】

一般にポリエステル、例えばポリエチレンテレフタレートは優れた力学特性を有しており、フィルム、繊維などの成形品として広く用いられている。

【0003】

通常、該ポリエステルは、成形品に易滑性を付与する目的でポリエステル中に炭酸カルシウム、シリカ、アルミナなどの不活性粒子を含有せしめ、成形品の表面に凹凸を付与する方法が行われている。

このような不活性粒子としては種々あるが、一般に不活性粒子はグリコールやポリエステルとの親和性に欠け、スラリー中やポリエステルの製造時に凝集してしまうという欠点があることが知られている。

ポリマ中に凝集粗大粒子が存在すると紡糸時に糸切れの原因となったり、またガイド、口金摩耗などの問題が生じ、フィルムにおいては、粗大突起、フィッシュアイ等の欠点の原因となり、特に磁気テープ用フィルムに適用する場合には、ドロップアウトや S/N 比の低下を引き起こしたり、耐摩耗性に劣るといった問題があった。

void fraction is 60% or more with mercury and helium substitution method of aluminum oxide particle and manufacturing method. of polyester composition which is stated in any of Claim 1~5 which is made feature

【Claim 7】

phosphorus compound and ammonia or lower amine compound in slurry, manufacturing method. of the polyester composition which is stated in any of Claim 1~6 which forms quaternary ammonium—phosphate or tertiary amine—phosphate and makes feature

【Description of the Invention】

【0001】

【Technological Field of Invention】

Being something regarding manufacturing method of polyester composition, furthermore details under specific condition dispersing aluminum oxide particle well, it combines the this invention, with state which it disperses in polyester satisfactorily, film or fiber which is superior in abrasion resistance it is obtained it regards method which produces polyester composition which is suited.

【0002】

【Prior Art】

Generally polyester, for example polyethylene terephthalate has had dynamic property which is superior, is used widely as film, fiber or other molded article.

【0003】

Usually, as for said polyester, with objective which grants slipperiness to molded article containing calcium carbonate, silica, alumina or other inactive particle in polyester, method which grants unevenness to surface of molded article is done.

There is a various, as this kind of inactive particle, but there is a deficiency that the inactive particle becomes insufficient generally in affinity of glycol and the polyester, in slurry and coheres when producing polyester, it is known.

When cohesion coarse particle exists in polymer, it becomes cause of yarn break at time of yarn-spinning, there was a problem that in addition guide and spinneret worn or other problem occur, become cause of coarse protuberance, fisheye or other deficiency regarding film, when it applies to especially for magnetic tape film, caused decrease of dropout and S/N ratio, are inferior to abrasion resistance.

## [0004]

従来からこれらの問題を解決すべく、スラリー調整時の分散効率を上げ、スラリーの分散性を向上する方法が提案されている(特開昭 53-114894 号公報、特開昭 53-124098 号公報、特開昭 53-125495 号公報など)。

## [0005]

しかしながら、これらの方法では、使用する分散媒と無機化合物粒子との親和性の問題からスラリー中やポリマ中で再凝集し、粗大粒子の生成を抑制することが十分ではなかった。

## [0006]

一方、表面処理剤を使用し、無機粒子のエチレングリコールスラリー中、ポリマ中での分散性向上を図る方法が提案されている(特公昭 45-32150 号公報、特公昭 45-32151 号公報、特開昭 51-68695 号公報、特開昭 54-131694 号公報、特開昭 53-45396 号公報、特開昭 56-88426 号公報、特開昭 63-221158 号公報、特開昭 63-280763 号公報)。

## [0007]

しかしながら、これらの方法では、重合反応時、表面処理剤の劣化によるポリマ品質の低下、異物の生成、ポリマ中での粒子の再凝集が生じ必ずしも十分な効果は得られていない。

さらに、重合反応時、表面処理剤の劣化によるポリマ品質の低下、粒子の再凝集を防止し、ポリマ中での分散性を図る方法が提案されている(特開昭 63-312345 号公報、特開昭 62-235353 号公報、特公平 6-72180 号公報)。

## [0008]

しかしながら、このような公知の方法をもってしても磁気テープのように繰り返し摩擦使用されるような場合には、粒子の分散性不良に起因して粒子の脱落を生じる。

## [0004]

From until recently, in order that these problem are solved, dispersion efficiency at time of slurry preparation is increased, method which improves hasbeen proposed dispersibility of slurry, (Japan Unexamined Patent Publication Showa 5 3- 114894 disclosure, Japan Unexamined Patent Publication Showa 5 3- 124098 disclosure, Japan Unexamined Patent Publication Showa 5 3- 125495 disclosure etc).

## [0005]

But, with these method, from problem of affinity of dispersion medium and inorganic compound particle which are used reaggregation it did in slurry and in the polymer, formation of coarse particle is controled was not fully .

## [0006]

On one hand, surface treatment agent is used, method which assures dispersibility improvement in ethylene glycol slurry of inorganic particle and in polymer is proposed, (Japan Examined Patent Publication Sho 45-32150 disclosure, Japan Examined Patent Publication Sho 45-32151 disclosure, Japan Unexamined Patent Publication Showa 5 1- 68695 disclosure, Japan Unexamined Patent Publication Showa 5 4- 1 31 694 disclosure, Japan Unexamined Patent Publication Showa 5 3- 45396 disclosure, Japan Unexamined Patent Publication Showa 56-88426 disclosure, Japan Unexamined Patent Publication Showa 6 3- 221158 disclosure, Japan Unexamined Patent Publication Showa 6 3- 280763 disclosure ).

## [0007]

But, with these method, at time of polymerization reaction, reaggregation of the particle in midst of decrease of polymer quality, formation and polymer of foreign matter occurs with deterioration of surface treatment agent and sufficient effectis not always acquired.

Furthermore, at time of polymerization reaction, reaggregation of decrease and the particle of polymer quality is prevented with deterioration of surface treatment agent, the method which assures dispersibility in polymer is proposed, (Japan Unexamined Patent Publication Showa 6 3- 31 2345 disclosure, Japan Unexamined Patent Publication Showa 6 2- 235353 disclosure, Japan Examined Patent Publication Hei 6-72180 disclosure ).

## [0008]

But, with this kind of known method doing like magnetic tape it repeats and it isrubbed is used it is kind of when, originating in dispersibility deficiency of the particle, it causes flaking of particle.



一方、フィルムの地肌を補強し粒子の脱落を防止するために特殊な粒子を使用することが提案されており、中でも酸化アルミニウム粒子が耐摩耗性に対する効果が大きいことが、特開平 2-129230 号公報(デルタ型酸化アルミニウム粒子)、特開平 2-38444 号公報(酸化アルミニウム粒子)などで提案されている。

しかしながら、上記したこれらの方法では酸化アルミニウム粒子の分散性が不十分であり、その結果としてフィルム、繊維などの成形品の耐摩耗性としても、いまだ十分なものが得られていなかった。

また、特開平 4-88016 号公報には二種類以上の酸化アルミニウム粒子を湿式分散処理する方法が提案されているが、混合条件によっては、粒子特性が異なることもあり凝集が起こりやすく該酸化アルミニウム粒子の分散性は不十分となり、その結果としてフィルム、繊維などの成形品の耐摩耗性も十分でなかった。

[0009]

【発明が解決しようとする課題】

本発明の目的は、前記した従来技術の欠点を解消することにより、特に二種以上の酸化アルミニウム粒子を用いた際に生じていた特有の再凝集の問題点を特定の分散条件を適用することによって解消し、ポリエステル中に良好に分散した状態で配合し、耐摩耗性に優れたフィルムあるいは繊維を得るに適したポリエステル組成物を得ることにある。

[0010]

【課題を解決するための手段】

前記した本発明の目的は、芳香族ジカルボン酸を主たる酸成分とし、脂肪族グリコールを主たるグリコール成分とするポリエステルを製造するに際し、重合反応の完結するまでの任意の時点で結晶構造の異なる少なくとも二種類以上の酸化アルミニウム粒子を溶媒の存在下、リン化合物およびアンモニア又は低級アミン化合物を添加して湿式分散処理したスラリーを添加することを特徴とする熱可塑性ポリエステル組成物の製造方法によって達成できる。

[0011]

【発明実施の形態】

On one hand, scalp of film is reinforced and uses special particle in order to prevent flaking of particle to be proposed, the effect aluminum oxide particle for abrasion resistance is large even among them, , the Japan Unexamined Patent Publication Hei 2- 129230 disclosure (delta type aluminum oxide particle ), it is proposed with Japan Unexamined Patent Publication Hei 2- 38444 disclosure (aluminum oxide particle ) etc.

But, with these method which were inscribed dispersibility of aluminum oxide particle being insufficient , as abrasion resistance of film、 fiber or other molded article as result, sufficient ones were not acquired yet.

In addition, method which wet type dispersing does aluminum oxide particle of two kinds or more to Japan Unexamined Patent Publication Hei 4- 88016 disclosure is proposed, but with mixing condition , cohesion to be easy to happen as for dispersibility of said aluminum oxide particle became insufficient partly due to fact that particle characteristic differs, either abrasion resistance of film、 fiber or other molded article was not fully as result.

[0009]

【Problems to be Solved by the Invention】

As for objective of this invention, before there are times when deficiency of Prior Art which was inscribed is cancelled, they cancel problem of peculiar reaggregation which it occurs occasion where aluminum oxide particle of especially 2 kinds or more is used specific dispersion condition is applied with, they combine with state which is dispersed in polyester satisfactorily, film or fiber which is superior in abrasion resistance is obtained at times when polyester composition which is suited is obtained.

[0010]

【Means to Solve the Problems】

When before objective of this invention which was inscribed designates the aromatic dicarboxylic acid as main acid component, produces polyester which designates aliphatic glycol as main glycol component, until polymerization reaction it completes, aluminum oxide particle above the at least two kinds where crystal structure differs in time point of option under existing of solvent, Adding phosphorus compound and ammonia or lower amine compound, it adds slurry which wet type dispersing it does it can achieve with manufacturing method of thermoplastic polyester composition which it makes feature.

[0011]

【Embodiment of the Invention】

本発明における二種以上の酸化アルミニウム粒子とは、従来よりよく知られている $\alpha$ 型酸化アルミニウム粒子、 $\gamma$ 型、 $\delta$ 型、 $\eta$ 型、 $\theta$ 型、 $\kappa$ 型、 $\chi$ 型などの活性酸化アルミニウム粒子、および非晶質の酸化アルミニウム粒子から選ばれるものである。

合成法に関しては種々の方法が公知であり、例えば、塩化アルミニウムに水素、酸素を吹き込んで気相中で加水分解すると $\delta$ 型酸化アルミニウムが、同じく塩化アルミニウムに水蒸気を吹き込んで気相中で加水分解すると非晶質酸化アルミニウムが、みょうばんの熱分解では、 $\gamma$ 型酸化アルミニウムが、みょうばんを炭酸塩中和後熱分解すると $\theta$ 型酸化アルミニウムができる。

また、通常のバイヤー法と呼ばれる方法では、 $\alpha$ 型酸化アルミニウムが生成し、主としてこのような結晶構造の決定には、これらの合成方法の選択と焼成温度、時間で左右される。

[0012]

なお、このような各種の酸化アルミニウム粒子の結晶構造は、通常の X 線回折分析によって同定することが可能である。

[0013]

このような酸化アルミニウム粒子群の中でも $\alpha$ 型、 $\gamma$ 型、 $\delta$ 型、 $\theta$ 型、などの活性酸化アルミニウム粒子から結晶構造の異なる二種類以上の酸化アルミニウム粒子を選択した場合、特に粒子の再凝集が生じ易いため本発明の分散方法による効果が大である。

その組み合わせは、任意であるが、例えば、 $\delta$ 型と $\gamma$ 型、 $\delta$ 型と $\theta$ 型、 $\gamma$ 型と $\theta$ 型、 $\alpha$ 型と $\delta$ 型と $\theta$ 型等である。

[0014]

酸化アルミニウムの二次粒子を構成する一次粒子は、BET 法による比表面積が  $10\text{ m}^2/\text{g}$  以上のものでフィルムまたは繊維の耐摩耗性の点で好ましく、更には、 $50\text{ m}^2/\text{g}$  以上、 $300\text{ m}^2/\text{g}$  以下が好ましい。

このような微細な粒子は非常に凝集しやすく、一般にはスラリーおよびポリマ中で凝集した二次粒子を形成している。

このような凝集が進むと、程度によっては粗大な粒子となり、フィルムあるいは繊維に用いる際には接触走行時にその部分が削られて脱落す

aluminum oxide particle of 2 kinds or more in this invention the;al which is well known from until recently -type aluminum oxide particle, the;ga -type, the;de -type, the;et -type, ;th type, ;ka type, is something which is chosen from the;ch type or other activity aluminum oxide particle, and aluminum oxide particle of amorphous.

various methods being public knowledge, blowing hydrogen, oxygen in for example aluminum chloride in regard to synthetic method, when hydrolysis it does in gas phase, the;de -type aluminum oxide, blowing water vapor similarly in aluminum chloride, when hydrolysis it does in gas phase, amorphous aluminum oxide, with thermal decomposition of alum, when the;ga -type aluminum oxide, after carbonate neutralizing thermal decomposition does alum, can do the;th type aluminum oxide.

In addition, with method which is called conventional Bayer process, the;al -type aluminum oxide forms, in decision of this kind of crystal structure, is influenced at selection and sintering temperature, time of these synthetic method mainly.

[0012]

Furthermore, identification it does crystal structure of this kind of various aluminum oxide particle, with conventional x-ray diffraction analysis, it is possible.

[0013]

When the;al -type, the;ga -type, the;de -type, aluminum oxide particle of two kinds or more where crystal structure differs from the;th type, or other activity aluminum oxide particle is selected even in this kind of aluminum oxide particle cluster, because reaggregation of especially particle is easy to occur, effect is large with dispersing method of this invention.

Combination is option, but for example ;de -type and the;ga -type, the;de -type and the;th type, ;ga -type and the;th type, ;al -type and it is the;de -type and a;th type etc.

[0014]

As for primary particle which forms secondary particle of aluminum oxide, with BET method specific surface area those of  $10\text{ m}^2/\text{g}$  or more is desirable in point of abrasion resistance of film or fiber, furthermore,  $50\text{ m}^2/\text{g}$  or more,  $300\text{ m}^2/\text{g}$  or less are desirable.

This kind of microscopic particle is easy to cohere very, generally slurry and the secondary particle which coheres in polymer forms.

When this kind of cohesion advances, case where it uses for the film or fiber with extent to become coarse, large particle, at time of contact running portion being shaved, there is a

るという欠点となり易い傾向にあるが、本発明により凝集が防止できる。

## [0015]

更に、酸化アルミニウム粒子は BET 法による全細孔容積が 0.2~1.5ml/g のものがフィルムまたは繊維の耐摩耗性の点で好ましく、更には、水銀およびヘリウム置換法による空隙率が60%以上であることが好ましい。

この理由は、酸化アルミニウムに細孔が存在したり、空隙が存在するとポリエステルとの親和性が良くなるために、粒子間の凝集が起こりにくくなるためと思われる。

## [0016]

本発明では、結晶構造の異なる少なくとも二種類以上の酸化アルミニウム粒子を、溶媒の存在下、リン化合物およびアンモニア又は低級アミン化合物を添加して湿式分散処理される。

これによって、粒子の均一分散が可能であり凝集して二次粒子を形成したとしてもその二次粒子径は非常に微細であり、粗大凝集塊もなく、よく分散された状態となる。

なお、ここでいう二次粒子径とは透過型電子顕微鏡で粒子を 1000 個観察した際の円相当平均径である。

## [0017]

この際の酸化アルミニウム粒子の混合比としては、全酸化アルミニウム粒子 100 重量部の中でそれぞれの酸化アルミニウム粒子が 10 重量部以上、更には 20 重量部以上であることが好ましい。

各酸化アルミニウム粒子の混合比が上記に満たない場合は、酸化アルミニウム粒子の分散が不十分となったり、スラリーおよびポリマ中で凝集し、工程通過性の低下や粗大粒子生成の原因となり好ましくない。

## [0018]

リン化合物およびアンモニア又は低級アミン化合物の酸化アルミニウム粒子に対する添加量は、それぞれ 0.5~10wt% が好ましく、更には、1~5wt% が好ましい。

また、溶媒の存在下湿式分散処理する際には、スラリーの粘度が高くなりすぎないよう適度な粘度とするため、酸化アルミニウム粒子の全濃度としては 1~50wt% が好ましく、更には、3~30wt% が好ましい。

tendency which is easy to become deficiency that flaking is done, it can prevent cohesion, but with this invention.

## [0015]

Furthermore, as for aluminum oxide particle with BET method total pore volume those of 0.2 -1.5 ml/g is desirable in point of abrasion resistance of film or the fiber, furthermore, void fraction is 60% or more with mercury and the helium substitution method, is desirable.

When as for this reason, capillary exists in aluminum oxide, empty gap exists, because affinity of polyester becomes good, cohesion between particle to happen is thought as for sake of it becomes difficult.

## [0016]

With this invention, aluminum oxide particle above at least two kinds where crystal structure differs, under existing of solvent, adding phosphorus compound and ammonia or the lower amine compound, wet type dispersing it is done.

Now, uniform dispersion of particle cohering, being possible, assuming that secondary particle was formed, secondary particle diameter very with fine, becomes state which is dispersed well without either coarse agglomerate.

Furthermore, secondary particle diameter referred to here case where particle 1000 is observed with transmission electron microscope it is a circular suitable average diameter.

## [0017]

In this case respective aluminum oxide particle 10 parts by weight or more, furthermore is 20 parts by weight or more in all aluminum oxide particle 100 parts by weight as proportion of aluminum oxide particle, it is desirable.

When proportion of each aluminum oxide particle is not full on description above, dispersion of aluminum oxide particle becomes insufficient, coheres in slurry and polymer, becomes cause of decrease and coarse particle formation of the process passing and is not desirable.

## [0018]

phosphorus compound and as for addition quantity for ammonia or lower amine compound aluminum oxide particle, 0.5 - 10 wt% are desirable respectively, furthermore, 1 - 5 wt% are desirable.

In addition, when under existing of solvent wet type dispersing doing, in order for viscosity of slurry not to become too high, in order to make suitable viscosity, 1 - 50 wt% are desirable as all concentration of aluminum oxide particle, furthermore, 3 - 30 wt% are desirable.

この際の溶媒としては、特に限定はないが、その後ポリエステルに添加することを考えると該ポリエステルの主原料および共重合成分などのグリコール成分が好ましい。

具体的には、エチレングリコール、テトラメチレングリコール、ヘキサメチレングリコール、ジエチレングリコール、プロピレングリコール、ブタンジオール、ネオペンチルグリコール、ポリオキシアルキレングリコール、p-キシリレングリコール、1,4-シクロヘキサジメタノール、5-ナトリウムスルホレゾルシン等が挙げられる。

この際の分散処理としては、通常の攪拌処理、超音波処理や媒体型の分散処理などが挙げられ、中でも、サンドグラインダーなどに代表される媒体型の分散処理が分散効率もよく好ましい。

[0019]

このように結晶構造の異なる二種類以上の酸化アルミニウム粒子を併用する場合、溶媒の存在下、リン化合物およびアンモニア又は低級アミン化合物を用いて湿式分散処理すると非常に分散性が良くなるため、その二次粒子径を、ポリエステル組成物からの成形品の目的に応じて任意に設定し制御することができる。

ポリエステル組成物をフィルムあるいは繊維に用いる際には、あまり大きすぎると粗大な突起が成形品に発生するために、二次粒子径は 5.0  $\mu\text{m}$  以下が好ましく、3.0  $\mu\text{m}$  以下がより好ましい。

また、0.01  $\mu\text{m}$  以上であることが製品の走行性向上の面で好ましい。

同様の理由で添加量も決定される。

すなわち、ポリエステル組成物をフィルムあるいは繊維に用いる際には、あまり添加量が多すぎると粗大な突起が成形品に発生したり作業性が低下するために、また添加量が少なすぎると十分な耐摩耗性が得られないために、酸化アルミニウム粒子の総添加量としては、ポリエステル 100 重量部に対して 0.01~30 重量部が好ましく、さらには 0.05~20 重量部が好ましい。

[0020]

本発明では、分散剤としてリン化合物およびアンモニア又は低級アミン化合物が用いられる。

リン化合物としては、リン酸、亜リン酸、ホスホン酸およびこれらの部分エステル化合物が好まし

In this case there is not especially limitation as solvent. After that when it adds to polyester you think, main raw material and copolymer component or other glycol component of said polyester are desirable.

Concretely, you can list ethyleneglycol, tetramethylene glycol, hexamethylene glycol, diethylene glycol and the propylene glycol, butanediol, neopentyl glycol, polyoxyalkylene glycol, p-xylylene glycol, 1,4-cyclohexane dimethanol, 5-sodium sulfo resorcinol etc.

In this case you can list conventional agitation, ultrasonic treatment and dispersing etc of medium type as dispersing, even among them, dispersing of medium type which is represented in sand grinder etc dispersion efficiency is desirable well.

[0019]

This way when aluminum oxide particle of two kinds or more where crystal structure differs is jointly used, when wet type dispersing it does under existing of solvent, making use of phosphorus compound and ammonia or lower amine compound because very the dispersibility becomes good, secondary particle diameter, to set to option according to the objective of molded article from polyester composition, it can control.

polyester composition case where it uses for film or fiber, when it is left over and is too large because coarse, large protuberance occurs in molded article, secondary particle diameter 5.0  $\mu\text{m}$  or less is desirable, 3.0  $\mu\text{m}$  or less are more desirable.

In addition, they are 0.01  $\mu\text{m}$  or greater, it is desirable in the aspect of running property improvement of product.

Also addition quantity is decided in similar reason.

namely, polyester composition case where it uses for film or fiber, when the addition quantity is many excessively, coarse, large protuberance occurs in molded article and/or when because workability decreases, in addition addition quantity is too little because sufficient abrasion resistance is not acquired, as total added quantity of aluminum oxide particle, 0.01 -30 parts by weight are desirable vis-a-vis polyester 100 parts by weight, Furthermore 0.05 - 20 parts by weight are desirable.

[0020]

With this invention, it can use phosphorus compound and ammonia or lower amine compound as the dispersant.

As phosphorus compound, phosphoric acid, phosphorous acid, phosphonic acid and these partial ester compound are

く、具体的には、リン酸、亜リン酸、リン酸モノエチルエステル、リン酸メチルエチルエステル、メチルホスホン酸、フェニルホスホン酸等を挙げることができる。

なかでもリン酸、亜リン酸、酸性リン酸エステルが取り扱いが容易である点で好ましい。

もちろんこれらのリン化合物の 2 種以上を併用してもかまわない。

アンモニア又は、低級アミン化合物としては、一般式  $R_1 R_2 R_3 N$  又は  $R_1 R_2 R_3 R_4 NX$  (式中  $R_1 \sim R_4$  は、水素基又は C5 以下の低級アルキル基、X は水酸基、ハロゲン等の対イオンを示す) で示される 1-4 級アミン化合物が使用され、具体的には、アンモニア、メチルエチルアミン、トリエチルアミン、テトラエチルアンモニウムハイドロキサイド、ジメチルプロピルアミン等を挙げることができる。

特に好ましいアミン化合物としては、第 3 級アミン、第 4 級アンモニウム化合物であり、具体的にはトリエチルアミン、テトラエチルアンモニウムハイドロキサイドである。

アルキル基の炭素数が 6 以上であると重合時ポリマの着色等の問題が生じ好ましくない。

リン化合物とアンモニアまたは低級アミン化合物の添加は、スラリー調整時に別々に又は同時に添加してもかまわないし、前もって適当な溶媒中で混合し、あるいは予めリン化合物と第 4 級アンモニウム化合物を反応させてテトラエチルアンモニウムリン酸塩として添加する方法も好適である。

好ましいリン化合物/アンモニアまたはアミン化合物のモル比は 5/1~1/5 であり、より好ましくは 2/1~1/4、最も好ましくは 1/1~1/3 である。

モル比を上記範囲とすると分散効果が十分得られ、ポリマ中での再凝集防止の効果が高い。

また、反応化合物を添加する場合の添加量は、0.5~5wt% とすると同様に分散効果が十分得られ、ポリマ中での再凝集防止の効果が高い。

[0021]

該スラリーをポリエステル重合反応系に添加する際の添加時期としてはポリエステルの重合反応の完結するまでの間の任意の時期であるが、エステル交換反応前から重縮合反応の減

desirable, concretely, can list phosphoric acid, phosphorous acid, monoethyl phosphate ester, methyl ethyl phosphate ester, methylphosphonic acid, phenyl phosphonic acid etc.

Even among them phosphoric acid, phosphorous acid, acidic phosphate ester it is desirable in point where handling is easy.

Of course jointly using 2 kinds or more of these phosphorus compound, you are not concerned.

As ammonia or lower amine compound, 1 - quaternary amine compound which is shown with General Formula  $R_1 R_2 R_3 N$  or  $R_1 R_2 R_3 R_4 NX$  (As for  $R_1 \sim R_4$  in Formula, as for lower alkyl group, X of hydrogen group or the C5 or less hydroxy group, halogen or other counterion is shown.) is used, concretely, can list ammonia, methylethyl amine and the triethylamine, tetraethyl ammonium hydroxide, dimethyl propyl amine etc.

Especially with tertiary amine, quaternary ammonium compound, it is a triethylamine, tetraethyl ammonium hydroxide concretely as desirable amine compound.

When carbon number of alkyl group is 6 or greater, when polymerizing the coloration or other problem of polymer occurs and is not desirable.

phosphorus compound and or adding separately simultaneously at time of the slurry preparation, you are not concerned ammonia or lower amine compound addition, it adds as tetraethyl ammonium phosphate also method where and, it mixes in advance in the suitable solvent, or beforehand phosphorus compound and quaternary ammonium compound reacts and is ideal.

mole ratio of desirable phosphorus compound/ammonia or amine compound with 5/1 - 1/5, is more preferably 2/1~1/4, most preferably 1/1~1/3.

When mole ratio is designated as above-mentioned range, dispersive effect is acquired fully, effect of reaggregation prevention in polymer is high.

In addition, as for addition quantity when reacted compound is added, when it makes 0.5 - 5 wt%, dispersive effect is acquired fully in same way, effect of reaggregation prevention in polymer is high.

[0021]

When adding said slurry to polymerization reaction system of polyester, until polymerization reaction of polyester it completes as addition time, it is a time of option between, but from before transesterification between to before start of

圧開始前までの間が粒子分散性の点で好ましい。

[0022]

本発明における芳香族ジカルボン酸成分としては、具体的にはテレフタル酸、イソフタル酸、ナフタレン-2,6-ジカルボン酸、5-ナトリウムスルホイソフタル酸等およびこれらのエステル形成性誘導体が挙げられる。

一方、本発明における脂肪族グリコール成分としては、具体的にはエチレングリコール、ジエチレングリコール、プロピレングリコール、ブタンジオール、テトラメチレングリコール、ヘキサメチレングリコール、ネオペンチルグリコール、ポリオキシアルキレングリコール等およびこれらのエステル形成性誘導体が挙げられる。

これらの芳香族ジカルボン酸と脂肪族グリコールからなるポリエステルとは、具体的にはポリエチレンテレフタレート、ポリブチレンテレフタレート、ポリエチレン-2,6-ナフタレートなどが挙げられる。

なお、該ポリエステルはホモポリエステルであっても少量であれば共重合成分を含んだコポリエステルであってもよく、この際の共重合成分の例としては、アジピン酸、セバシン酸、フタル酸、イソフタル酸、ナフタレン-2,6-ジカルボン酸、5-ナトリウムスルホイソフタル酸等のジカルボン酸成分、トリメリット酸、ピロメリット酸等の多価カルボン酸成分、およびテトラメチレングリコール、ヘキサメチレングリコール、ジエチレングリコール、プロピレングリコール、ネオペンチルグリコール、ポリオキシアルキレングリコール、p-キシリレングリコール、1,4-シクロヘキサジメタノール、5-ナトリウムスルホレゾルシン等のジオール成分が挙げられる。

[0023]

このようなポリエステルの重合度としては、o-クロルフェノールに溶解させて測定した極限粘度として $[\eta]$ が0.30以上が好ましい。

またポリエステル中のカルボキシル末端基としては20eq/t~100eq/tが好ましい。

なお必要に応じて抗酸化剤などを添加しても構わない。

[0024]

【実施例】

以下に実施例を挙げて本発明を詳細に説明する。

pressure reduction of the condensation polymerization is desirable in point of particle dispersability.

[0022]

Concretely terephthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, 5-sodium sulfo isophthalic acid etc and you can list these ester-forming derivative as aromatic dicarboxylic acid component in this invention.

On one hand, concretely ethyleneglycol, diethylene glycol, propylene glycol, butanediol, tetramethylene glycol, hexamethylene glycol and the neopentyl glycol, polyoxyalkylene glycol etc and you can list these ester-forming derivative as aliphatic glycol component in this invention.

These aromatic dicarboxylic acid and polyester which consists of aliphatic glycol, you can list polyethylene terephthalate, polybutylene terephthalate, polyethylene-2,6-naphthalate etc concretely.

Furthermore, if said polyester and is trace with homopolyester, it is good with copolyester which includes copolymer component, in this case adipic acid, sebacic acid, phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, 5-sodium sulfo isophthalic acid or other dicarboxylic acid component, trimellitic acid, pyromellitic acid or other polybasic carboxylic acid component, and tetramethylene glycol, hexamethylene glycol and diethylene glycol, it can list propylene glycol, neopentyl glycol, polyoxyalkylene glycol, p-xylylene glycol, 1,4-cyclohexane dimethanol, 5-sodium sulfo resorcinol or other diol component as example of copolymer component.

[0023]

Melting in o-chloro phenol as degree of polymerization of this kind of polyester,  $[\eta]$  0.30 or greater is desirable as intrinsic viscosity which it measured.

In addition 20 eq/ton~100 eq/ton are desirable as carboxyl endgroup in polyester.

Furthermore it is possible to add according to need antioxidant etc.

[0024]

[Working Example(s)]

Listing Working Example below, you explain this invention in detail.

なお、本発明に用いた各特性の測定方法は次のとおりである。

[0025]

(1)酸化アルミニウム粒子の比表面積の評価

通常の B.E.T.法に従って測定( $\text{m}^2/\text{g}$ )した。

[0026]

(2)酸化アルミニウム粒子の二次粒子径の評価

酸化アルミニウム粒子をポリエステル中に配合せしめ、 $0.2\mu\text{m}$  厚みの超薄切片にカッティング後、透過型電子顕微鏡で観察し、凝集状態の二次粒子 1000 個の面積平均径( $\mu\text{m}$ )で評価した。

[0027]

(3)酸化アルミニウム粒子の全細孔容積の評価

通常の B.E.T.法に従って測定( $\text{ml/g}$ )した。

[0028]

(4)酸化アルミニウム粒子の空隙率の評価

通常の水銀およびヘルウム置換法に従って測定(%)した。

[0029]

(5)耐摩耗性の評価

得られたポリエステル組成物を実施例に示す方法で二軸延伸フィルムとし細幅にスリットしたテープ状ロールをステンレス鋼 SUS-304 製ガイドロールに  $200\text{g}/1/2\text{inch}$  一定張力( $200\text{g}/1/2\text{inch}$ )で高速( $250\text{m}/\text{min}$ )、長さ  $200\text{m}$  こすりつけ、ガイドロール表面に発生する白粉量によって、次のようにランク付けし、2 級までを合格とした。

[0030]

1 級.....白粉の発生まったくなし

2 級.....白粉の発生少しあり

3 級.....白粉の発生かやや多い

4 級.....白粉の発生かなり多い

[0031]

Furthermore, measurement method of each characteristic which is used for this invention is as follows.

[0025]

evaluation of specific surface area of (1) aluminum oxide particle

Following to conventional BET method, it measured ( $\text{m}^2/\text{g}$ ).

[0026]

evaluation of secondary particle diameter of (2) aluminum oxide particle

Combining aluminum oxide particle in polyester, in ultrathin slice of  $0.2\mu\text{m}$  thick after cutting, you observed with transmission electron microscope, secondary particle 1000 of agglomerated state the evaluation did with surface area average diameter ( $\mu\text{m}$ ).

[0027]

evaluation of total pore volume of (3) aluminum oxide particle

Following to conventional BET method, it measured ( $\text{ml/g}$ ).

[0028]

evaluation of void fraction of (4) aluminum oxide particle

To conventional mercury and following to jpl1 ウム substitution method, it measured (%).

[0029]

evaluation of (5) abrasion resistance

It made biaxially drawn film with method which shows polyester composition which it acquires in Working Example in narrow in stainless steel SUS-304 make guide roll high speed ( $250\text{m}/\text{min}$ ), length  $200\text{m}$  it was accustomed to rubbing tape roll which slit is done with  $200\text{g}/1/2\text{inch}$  constant tension ( $200\text{g}/1/2\text{inch}$ ), at white powder quantity which occurs in the guide roll surface, following way ranking it did, to secondary passing made.

[0030]

Occurrence of primary.....white powder completely none

Occurrence of secondary.....white powder a little to be

Occurrence mosquito net of terniery.....white powder and many

Occurrence of quaternary.....white powder quite many

[0031]

## (4)表面凹凸の評価

得られたポリエステル組成物を公知の方法で二軸延伸フィルムとし、JISB0601に準じサーフコム表面粗さ計を用い、針径  $2\mu\text{m}$ 、荷重 70mg、測定基準長 0.25mm、カットオフ 0.08mm の条件下で中心線平均粗さ(Ra)を測定した。

[0032]

## 実施例 1

B.E.T.比表面積  $100\text{m}^2/\text{g}$  の  $\delta$  型酸化アルミニウム粒子 4 重量部、B.E.T.比表面積  $85\text{m}^2/\text{g}$  の  $\theta$  型酸化アルミニウム粒子 6 重量部、エチレングリコール 90 重量部、全酸化アルミニウム粒子に対してテトラエチルアンモニウムリン酸塩 5Wt% を添加し、混合してサンドグライNDERを用いて分散処理し、 $\delta$  型酸化アルミニウム粒子/ $\theta$  型酸化アルミニウム粒子/エチレングリコールスラリー(A)100 重量部を得た。

[0033]

他方、ジメチルテレフタレート 100 重量部、エチレングリコール 64 重量部に触媒として酢酸マンガ 0.04 重量部を加えてエステル交換反応を行った後、反応生成物に先に調製したスラリー(A)5 重量部と触媒の酸化アンチモン 0.03 重量部および耐熱安定剤としてトリメチルホスフェート 0.03 重量部を加え、重縮合反応を行い、極限粘度 0.617 のポリエチレンテレフタレート組成物を得た。

透過型電子顕微鏡による酸化アルミニウム粒子の二次粒子径は、 $0.14\mu\text{m}$  であった。

[0034]

このポリエチレンテレフタレート組成物を 290 deg C で溶融押し出しし、その後 90 deg C で縦横それぞれ 3 倍延伸し、さらにその後 220 deg C で 15 秒熱処理し、厚さ  $15\mu\text{m}$  のポリエチレンテレフタレート二軸延伸フィルムを得た。

[0035]

このフィルムを評価したところ  $Ra=0.011\mu\text{m}$ 、耐摩耗性評価 1 級であり、耐摩耗性に非常に優れたフィルムであった。

[0036]

## 実施例 2~5

ポリエチレンテレフタレート組成物中の酸化アルミニウム粒子の種類、比表面積、二次粒子径、

## evaluation of (4) surface unevenness

polyester composition which it acquires was designated as biaxially drawn film with the known method, center-line average surface roughness (Ra) was measured under condition of needle diameter  $2\mu\text{m}$ , load 70 mg, measurement reference length 0.25 mm, cut off 0.08 mm making use of Surfcom surface roughness gauge according to JIS B0601.

[0032]

## Working Example 1

It added tetraethyl ammonium phosphate 5Wt% the;de of B.E.T. specific surface area  $100\text{m}^2/\text{g}$  -type aluminum oxide particle 4 parts by weight, B.E.T. specific surface area  $85\text{m}^2/\text{g}$  vis-a-vis the;th type aluminum oxide particle 6 parts by weight, ethyleneglycol 90 parts by weight, all aluminum oxide particle, mixed and dispersing it did making use of sand grinder, the;de-type aluminum oxide particle/ the;th type aluminum oxide particle/ethylene glycol slurry (A) acquired 100 parts by weight.

[0033]

To other, dimethyl terephthalate 100 parts by weight, ethyleneglycol 64 parts by weight as catalyst after doing transesterification including manganese acetate 0.04 parts by weight, condensation polymerization was done including trimethyl phosphate 0.03 parts by weight slurry which is manufactured first in reaction product (A) as 5 parts by weight and antimony oxide 0.03 parts by weight and heat resistant stabilizer of the catalyst, polyethylene terephthalate composition of intrinsic viscosity 0.617 was acquired.

secondary particle diameter of aluminum oxide particle was  $0.14\mu\text{m}$  with transmission electron microscope.

[0034]

melt extrusion it did this polyethylene terephthalate composition with 290 deg C, after that longitudinal and transverse 3 times drew respectively with 90 deg C, furthermore after that 15 second thermal processing did with 220 deg C, acquired polyethylene terephthalate biaxially drawn film of thickness  $15\mu\text{m}$ .

[0035]

When evaluation it does this film with  $Ra=0.011\mu\text{m}$ , abrasion resistance evaluation primary, it was a film which is superior very in abrasion resistance.

[0036]

## Working Example 2~5

types, specific surface area, secondary particle diameter, addition quantity and proportion of aluminum oxide particle



添加量および混合比を変更し、実施例 1 と同様の方法で二軸延伸ポリエステルフィルムを得た。

これらのフィルムの評価結果を表 1 に示したが、耐摩耗性に非常に優れたフィルムであった。

[0037]

#### 実施例 6

B.E.T.比表面積  $98\text{m}^2/\text{g}$  の  $\delta$  型酸化アルミニウム粒子 5 重量部、B.E.T.比表面積  $120\text{m}^2/\text{g}$  の  $\gamma$  型酸化アルミニウム粒子 3 重量部、B.E.T.比表面積  $85\text{m}^2/\text{g}$  の  $\theta$  型酸化アルミニウム粒子 2 重量部を混合する以外は実施例 1 と同様の方法で分散処理し、 $\delta$  型酸化アルミニウム粒子/ $\gamma$  型酸化アルミニウム粒子/ $\theta$  型酸化アルミニウム粒子/エチレングリコールスラリー(B)100 重量部を得た。

[0038]

該エチレングリコールスラリー(B)を実施例 1 と同様の方法でポリエステル重合反応系に添加し、重合反応を行い、固有粘度 0.618 のポリエチレンテレフタレート組成物を得た。

透過型電子顕微鏡による二次粒子径は、 $0.14\mu\text{m}$  であった。

該ポリエチレンテレフタレート組成物を用いて実施例 1 と同様の方法で二軸延伸ポリエステルフィルムを得た。

[0039]

このフィルムを評価したところ  $R_a=0.010\mu\text{m}$ 、耐摩耗性評価 1 級であり、耐摩耗性に非常に優れたフィルムであった。

[0040]

#### 比較実施例 1

B.E.T.比表面積  $100\text{m}^2/\text{g}$  の  $\delta$  型酸化アルミニウム粒子 10 重量部、エチレングリコール 90 重量部を混合してサンドグラインダーを用いて分散処理し、 $\delta$  型酸化アルミニウム粒子/エチレングリコールスラリー(C)100 重量部を得た。

[0041]

他方、ジメチルテレフタレート 100 重量部、エチレングリコール 64 重量部に触媒として酢酸マンガン 0.04 重量部を加えてエステル交換反応を行った後、反応生成物に先に調製したスラリー(C)5 重量部と触媒の酸化アンチモン 0.03 重量

in polyethylene terephthalate composition were modified, the biaxially drawn polyester film was acquired with method which is similar to Working Example 1.

evaluation result of these film was shown in Table 1, but it was a film which is superior very in abrasion resistance.

[0037]

#### Working Example 6

The;de of B.E.T. specific surface area  $98\text{m}^2/\text{g}$  -type aluminum oxide particle 5 parts by weight, B.E.T. specific surface area  $120\text{m}^2/\text{g}$  the;ga other than -type aluminum oxide particle 3 parts by weight, B.E.T. specific surface area  $85\text{m}^2/\text{g}$  mixes the;th type aluminum oxide particle 2 parts by weight, dispersing it did with method which is similar to Working Example 1,the;de -type aluminum oxide particle/the;ga -type aluminum oxide particle/ the;th type aluminum oxide particle/ethylene glycol slurry (B ) acquired 100 parts by weight.

[0038]

said ethylene glycol slurry (B ) was added to polyester condensation polymerization system with method which is similar to Working Example 1; condensation polymerization was done, polyethylene terephthalate composition of inherent viscosity 0.618 was acquired.

secondary particle diameter was  $0.14\mu\text{m}$  with transmission electron microscope .

biaxially drawn polyester film was acquired with method which is similar to Working Example 1 making use of said polyethylene terephthalate composition.

[0039]

When evaluation it does this film with  $R_a=0.010\mu\text{m}$ , abrasion resistance evaluation primary , it was a film which is superior very in abrasion resistance.

[0040]

#### Comparative Working Example 1

The;de of B.E.T. specific surface area  $100\text{m}^2/\text{g}$  mixing -type aluminum oxide particle 10 parts by weight, ethyleneglycol 90 parts by weight, dispersing it did making use of the sand grinder, the;de -type aluminum oxide particle/ethylene glycol slurry (C ) acquired 100 parts by weight.

[0041]

To other, dimethyl terephthalate 100 parts by weight, ethyleneglycol 64 parts by weight as catalyst after doing transesterification including manganese acetate 0.04 parts by weight,condensation polymerization was done including trimethyl phosphate 0.03 parts by weight slurry which is

部および耐熱安定剤としてトリメチルホスフェート 0.03 重量部を加え、重縮合反応を行い、固有粘度 0.619 のポリエチレンテレフタレート組成物を得た。

透過型電子顕微鏡による二次粒子径は、0.18  $\mu\text{m}$  であった。

#### [0042]

このポリエチレンテレフタレート組成物を 290 deg C で溶融押し出し、その後 90 deg C で縦横それぞれ 3 倍延伸し、さらにその後 220 deg C で 15 秒熱処理し、厚さ 15  $\mu\text{m}$  のポリエチレンテレフタレート二軸延伸フィルムを得た。

#### [0043]

このフィルムを評価したところ  $R_a=0.011 \mu\text{m}$ 、耐摩耗性評価 3 級であり、必ずしも耐摩耗性が満足できるフィルムではなかった。

#### [0044]

##### 比較実施例 2~5

ポリエチレンテレフタレート中の酸化アルミニウム粒子の種類、比表面積、二次粒子径および添加量を変更し、比較実施例 1 と同様の方法で二軸延伸ポリエステルフィルムを得た。

これらのフィルムの評価結果を表 2 に示したが、耐摩耗性が満足できるフィルムではなかった。

#### [0045]

##### 比較実施例 6

比較実施例 1 において、分散剤として水酸化テトラエチルアンモニウムを用いる以外は同様にして、極限粘度 0.616 のポリエチレンテレフタレート組成物を得た。

透過型電子顕微鏡による二次粒径は 0.22  $\mu\text{m}$  であった。

該ポリエチレンテレフタレート組成物を用いて比較実施例 1 と同様の方法で二軸延伸ポリエステルフィルムを得た。

このフィルムを評価したところ  $R_a=0.013 \mu\text{m}$ 、耐摩耗性評価 3 級であり、耐摩耗性において満足できるフィルムではなかった。

#### [0046]

##### 比較実施例 7

比較実施例 2 において、分散剤としてヘキサメタリン酸ソーダを用いる以外は同様にして、表 3 に

manufactured first in reaction product (C) as 5 parts by weight and antimony oxide 0.03 parts by weight and heat resistant stabilizer of the catalyst, polyethylene terephthalate composition of inherent viscosity 0.619 was acquired.

secondary particle diameter was 0.18  $\mu\text{m}$  with transmission electron microscope.

#### [0042]

With 290 deg C melt extrusion, after that longitudinal and transverse 3 times drawing this polyethylene terephthalate composition respectively with 90 deg C, furthermore after that 15 second thermal processing it did with 220 deg C, acquired polyethylene terephthalate biaxially drawn film of thickness 15  $\mu\text{m}$ .

#### [0043]

When evaluation it does this film with  $R_a=0.011 \mu\text{m}$ , abrasion resistance evaluation ternary, it was not a film which always can be satisfied abrasion resistance.

#### [0044]

##### Comparative Working Example 2~5

types, specific surface area, secondary particle diameter and addition quantity of aluminum oxide particle in polyethylene terephthalate were modified, the biaxially drawn polyester film was acquired with method which is similar to Comparative Working Example 1.

evaluation result of these film was shown in Table 2, but it was not a film which can be satisfied abrasion resistance.

#### [0045]

##### Comparative Working Example 6

Other than using tetraethyl ammonium hydroxide in Comparative Working Example 1, as dispersant, polyethylene terephthalate composition of intrinsic viscosity 0.616 was acquired with as similar.

secondary particle diameter was 0.22  $\mu\text{m}$  with transmission electron microscope.

biaxially drawn polyester film was acquired with method which is similar to Comparative Working Example 1 making use of said polyethylene terephthalate composition.

When evaluation it does this film with  $R_a=0.013 \mu\text{m}$ , abrasion resistance evaluation ternary, it was not a film which it can be satisfied in abrasion resistance.

#### [0046]

##### Comparative Working Example 7

Other than using sodium hexametaphosphate in Comparative Working Example 2, as dispersant, as stated in Table 3 with

記載の様に固有粘度 0.616 のポリエチレンテレフタレート組成物を得た。

透過型電子顕微鏡による二次粒子径は、0.22  $\mu\text{m}$  であった。

該ポリエチレンテレフタレート組成物を用いて比較実施例 1 と同様の方法で二軸延伸ポリエステルフィルムを得た。

このフィルムを評価したところ  $R_a=0.013 \mu\text{m}$ 、耐摩耗性評価 3 級であり、耐摩耗性において満足できるフィルムではなかった。

[0047]

実施例 7~10

ポリエチレンテレフタレート中の酸化アルミニウム粒子の種類、比表面積、二次粒子径および添加量を変更し、実施例 1 と同様の方法で二軸延伸ポリエステルフィルムを得た。

これらのフィルムの評価結果を表 1 に示した。

耐摩耗性に優れ、合格範囲のフィルムであった。

[0048]

[表 1]

as similar, polyethylene terephthalate composition of inherent viscosity 0.616 was acquired.

secondary particle diameter was 0.22  $\mu\text{m}$  with transmission electron microscope.

biaxially drawn polyester film was acquired with method which is similar to Comparative Working Example 1 making use of said polyethylene terephthalate composition.

When evaluation it does this film with  $R_a=0.013 \mu\text{m}$ , abrasion resistance evaluation terniery, it was nota film which it can be satisfied in abrasion resistance.

[0047]

Working Example 7~10

types, specific surface area, secondary particle diameter and addition quantity of aluminum oxide particle in polyethylene terephthalate were modified, the biaxially drawn polyester film was acquired with method which is similar to Working Example 1.

evaluation result of these film was shown in Table 1.

It was superior in abrasion resistance, it was a film of passing range.

[0048]

[Table 1]

No	酸化アルミニウムスラリー			ポリエステル		フィルム特性		
	種 (結晶)	比表面積 ( $m^2/g$ )	割合	リン-アミン 化合物	ポリエステルへの スチール被覆量 ( $\mu m$ )	2次被覆 ポリマー被覆量 ( $\mu m$ )	Ra( $\mu m$ )	耐摩耗性
実施例 1	$\delta/\theta$	100/85	4/6	テトラエチルアンモニウムリン酸塩	5	0.14	0.617	1級
実施例 2	$\delta/\theta$	100/100	5/5	テトラエチルアンモニウムリン酸塩	5	0.13	0.621	1級
実施例 3	$\delta/\theta$	100/100	1/9	テトラエチルアンモニウムリン酸塩	5	0.14	0.619	1級
実施例 4	$\delta/\theta$	100/100	9/1	テトラエチルアンモニウムリン酸塩	5	0.12	0.613	1級
実施例 5	$\delta/\gamma$	100/130	5/5	テトラエチルアンモニウムリン酸塩	5	0.15	0.616	1級
実施例 6	$\delta/\gamma/\theta$	98/120/85	5/3/2	テトラエチルアンモニウムリン酸塩	5	0.15	0.616	1級
実施例 7	$\delta/\theta$	100/30	0.5/9.5	テトラエチルアンモニウムリン酸塩	5	0.21	0.625	2級
実施例 8	$\delta/\theta$	30/100	0.2/9.8	テトラエチルアンモニウムリン酸塩	5	0.20	0.609	2級
実施例 9	$\delta/\alpha$	100/10	9.5/0.5	テトラエチルアンモニウムリン酸塩	5	0.21	0.611	2級
実施例 10	$\delta/\gamma$	100/20	9.8/0.2	テトラエチルアンモニウムリン酸塩	5	0.20	0.606	2級
比較実施例 1	$\delta$	100	10	なし	5	0.18	0.619	3級
比較実施例 2	$\delta/\theta$	100/100	5/5	なし	5	0.19	0.619	3級
比較実施例 3	$\delta/\theta$	100/100	5/5	なし	5	0.21	0.616	3級
比較実施例 4	$\delta/\theta$	100/100	9/1	なし	5	0.18	0.615	3級
比較実施例 5	$\delta/\gamma$	100/130	5/5	なし	5	0.22	0.621	4級
比較実施例 6	$\delta$	100	10	複合テトラエチルアンモニウムリン酸塩	5	0.22	0.616	3級
比較実施例 7	$\delta/\theta$	100/100	5/5	ヘキサタリリン酸塩	5	0.22	0.616	3級

[0049]

【発明の効果】

[0049]

[Effects of the Invention]

本発明のポリエステル組成物の製造方法は、結晶構造の異なる特に極微細な二種類以上の酸化アルミニウム粒子を併用し、リン化合物およびアンモニア又は低級アミン化合物を添加して湿式分散処理して分散させ、スラリー中に良好に分散した状態でポリエステル重合反応系に添加されるため、これによって得られたポリエステル組成物は、耐摩耗性に優れたフィルムあるいは繊維およびその他の成形品を得るに適しており、特に繰り返し摩擦使用される磁気テープに好ましく用いることができる。

manufacturing method of polyester composition of this invention jointly using aluminum oxide particle of the especially ultrafine two kinds or more where crystal structure differs, adding phosphorus compound and the ammonia or lower amine compound and wet type dispersing doing dispersing, because it is added to polyester polymerization reaction system with state which it disperses in the slurry satisfactorily, as for polyester composition which it acquires with this, film or fiber and other molded article which are superior in the abrasion resistance are obtained to be suitable, especially it repeats and it can use for magnetic tape which it is rubbed is used desirably.

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## Abstract

(57)[要約]

(57) [Abstract]

[課題]

[Problems to be Solved by the Invention]

ポリエステル中の異物数、色相を良好なレベルに制御した、従来にないほど、表面欠点が少なく、色相も良好な成形加工品を成形できる芳香族ポリエステル、及び該ポリエステルを使用し、従来にないほど表面欠点が少なく、色相も良好な二軸延伸ポリエステルフィルムを提供する。

Extent and surface deficiency which controlled amount of foreign matter, hue in polyester in the satisfactory level, are not former are small, hue the satisfactory molded article aromatic polyester, and said polyester which it can form are used, extent surface deficiency which is not former is little, also hue offers satisfactory biaxially drawn polyester film.

[解決手段]

[Means to Solve the Problems]

Sb 化合物を重合触媒として重合した芳香族ポリエステル、特にエチレンテレフタレートの主たる繰り返し単位とするポリエステルであり、極限粘度数が 0.4-1.5 の範囲にあり、Sb 化合物のポリマー中の量が Sb 原子量換算で 50-400ppm であり、該ポリマー 1g 中の 10 $\mu$ m 以上の大きさの異物数が 50 個以下で、Lab 法により測定されたカラーの L 値と b 値が下式(1)、(2)を満たす芳香族ポリエステルおよび、これからなる二軸延伸フィルム。

With polyester which designates aromatic polyester, especially ethylene terephthalate which polymerized Sb compound as polymerization catalyst as main repeat unit, limiting viscosity to be 0.4 - 1.5 ranges, quantity in polymer of Sb compound being Sb atomic weight conversion and with 50 - 400 ppm, amount of foreign matter of size of 10 $\mu$ m or greater in said polymer 1g being 50 or less, L value and b value of color which was measured by Lab method formula below (1), aromatic polyester which fills up (2) and biaxially drawn film. which consists of this

75 ≤ L - b			(1)
75 ≤ L - b			(1)
b ≤ 3			(2)
b ≤ 3			(2)

## Claims

[特許請求の範囲]

[Claim(s)]

[請求項 1]

[Claim 1]

Sb 化合物を重合触媒として重合した芳香族ポリエステルであり、極限粘度数が 0.4-1.5 の範囲にあり、該ポリエステル中の Sb 化合物の量が Sb 原子量換算で 50-400ppm であり、10 $\mu$ m 以上の大きさの異物数がポリエステル 1g 当たり 50 個以下であり、かつ Lab 法により測定されたカラーの L 値と b 値が下式(1)、(2)を満足することを特徴とする芳香族ポリエステル。

With aromatic polyester which polymerized Sb compound as polymerization catalyst, limiting viscosity are 0.4 - 1.5 ranges, quantity of Sb compound in said polyester being Sb atomic weight conversion and with 50 - 400 ppm, amount of foreign matter of size of 10 $\mu$ m or greater being polyester per gram 50 or less, L value and b value of color which was measured at same time by Lab method formula below (1), satisfy (2) aromatic polyester. which is made feature

[数 1]

[Mathematical Formula 1]

75 ≤ L - b			(1)
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75 <= L - b、			(1)
b ≤ 3			(2)
b □ 3			(2)

## 【請求項 2】

芳香族ポリエステルがエチレンテレフタレートの主たる繰返し単位とするポリエステルである請求項 1 記載の芳香族ポリエステル。

## 【請求項 3】

請求項 1 記載の芳香族ポリエステルからなる二軸延伸ポリエステルフィルム。

## Specification

## 【発明の詳細な説明】

## 【0001】

## 【発明の属する技術分野】

本発明は芳香族ポリエステルおよび二軸延伸ポリエステルフィルムに関し、更に詳しくはポリマー中の異物が少なく且つ着色が少なくカラー(色相)に優れ、さらに成形性、成形品品質に優れた芳香族ポリエステルおよびこれからなる二軸延伸フィルムに関する。

## 【0002】

## 【従来の技術】

ポリエチレンテレフタレートに代表される芳香族ポリエステルは力学特性、耐熱性、耐候性、耐電気絶縁性、耐薬品性に優れ、フィルム、繊維、ボトル、その他の成形品として広く使用されている。

## 【0003】

かかるポリエステルは各用途において要求特性が異なるが、その製造にあたっては、重合反応を円滑に進行させるために重合触媒が用いられる。

この重合触媒としては種々の金属化合物が知られているが、中でも三酸化アンチモンの如きアンチモン(Sb)化合物は安価且つ高い重合活性を持つ触媒として広く使用されている。

## 【0004】

しかしながら、Sb 化合物も問題を抱えている。

たとえば、Sb 化合物はその一部が反応中に還元されて金属 Sb やその他異物を生成し、ポリマ

## 【Claim 2】

aromatic polyester, which is stated in Claim 1 which is a polyester where the aromatic polyester designates ethylene terephthalate as main repeat unit

## 【Claim 3】

biaxially drawn polyester film, which consists of aromatic polyester which is stated in Claim 1

## 【Description of the Invention】

## 【0001】

## 【Technological Field of Invention】

this invention regards aromatic polyester and biaxially drawn polyester film, furthermore as for details foreign matter in polymer and coloring is superior little little in the color (hue), furthermore regards aromatic polyester which is superior in moldability, molded article quality and biaxially drawn film which consists of this.

## 【0002】

## 【Prior Art】

aromatic polyester which is represented in polyethylene terephthalate is superior in dynamic property, heat resistance, antiweathering agent, electrical resistance, chemical resistance, is used widely as film, fiber, bottle, other molded article.

## 【0003】

required property it differs as for this polyester in each application it can use the polymerization catalyst in order to advance polymerization reaction smoothly, but at time of the production.

various metal compound is known as this polymerization catalyst, but antimony (Sb) compound like the antimony trioxide even among them is used widely inexpensive and as catalyst which has high polymerization activity.

## 【0004】

But, also Sb compound has held problem.

for example Sb compound part of that being reduced while reacting, forms the metal Sb and in addition foreign matter,

一の色を黒くせたり、工程調子を悪化させたり、成形品品質を悪化させたりする。

[0005]

従来から、重合触媒に Sb 化合物を用いたポリマーの異物減少については様々な検討がなされてきた。

たとえば、特開平 1-275628 号公報、特開平 2-3420 号公報には、エステル交換(EI)法において Sb 化合物を EI 反応初期に添加し、EI 及び重縮合反応の両方の触媒として利用することが提案され、別の EI 触媒が添加されていない分だけポリマー中の異物が少なくなる事が記載されている。

しかし、本発明者の検討によれば、このような重合法によって得られるポリマーは、重合触媒として用いる Sb 化合物に起因する異物数の低減や着色防止には効果が少なく、良好な品質のポリマーを得ることが難しいことが明らかになった。

また、特開昭 61-231025 号公報には、Sb 化合物を重合触媒に使用し、重縮合反応の後半にテレフテル酸を少量添加して、紡糸時の口金に堆積する異物を減少させる技術が提案されている。

しかし、この技術を用いてもポリマー中の異物は十分に減少せず、良好なポリマー品質を得ることが難しい。

更にまた、特開昭 54-39490 号公報、特開昭 60-67529 号公報には、Sb 化合物とリン化合物を予め適当な条件で加熱混合したものを重縮合触媒に用いることが提案されているが、この効果も紡糸中の口金異物の低減にとどまり、ポリマー中異物の低減効果は期待できない。

[0006]

[発明が解決しようとする課題]

本発明の目的は、ポリエステル中の異物数、色相を良好なレベルに制御した、従来にないほど、表面欠点が少ない、色相も良好な成形加工品を成形できる芳香族ポリエステルを提供することにある。

本発明の他の目的は、前記ポリエステルを使用した、従来にないほど表面欠点が少ない、色相も良好な二軸延伸ポリエステルフィルムを提供す

blackens color of polymer, the process condition deteriorates, molded article quality deteriorates.

[0005]

From until recently, you did various examination concerning foreign matter decrease of polymer which uses Sb compound for polymerization catalyst.

It adds Sb compound to EI reaction initial stage in for example Japan Unexamined Patent Publication Hei 1- 275628 disclosure, Japan Unexamined Patent Publication Hei 2- 3420 disclosure in ester exchange (EI) method, it utilizes to be proposed, as catalyst of both of the EI and condensation polymerization equal to amount where another EI catalyst is not added foreign matter in polymer decreasing is stated.

But, according to examination of this inventor, as for polymer which is acquired with this kind of polymerization method, effect is little in decrease and coloring prevention of amount of foreign matter which originates in Sb compound which it uses as polymerization catalyst polymer of satisfactory quality is obtained, is difficult, it became clear.

In addition, Sb compound is used for polymerization catalyst in Japan Unexamined Patent Publication Showa 61- 231025 disclosure, terephthalic acid trace addition is done in last half of condensation polymerization, technology which decreases foreign matter which is accumulated in spinneret at the time of yarn-spinning is proposed.

But, it does not decrease foreign matter in polymer to fully making use of this technology, obtains satisfactory polymer quality it is difficult.

Furthermore and, those which beforehand it heats mix Sb compound and the phosphorus compound with suitable condition are used for condensation catalyst in Japan Unexamined Patent Publication Showa 54- 39490 disclosure, Japan Unexamined Patent Publication Showa 60-67529 disclosure, it is proposed, but also this effect is restricted to decrease of spinneret foreign matter in yarn-spinning, you cannot expect reducing effect of foreign matter in polymer.

[0006]

[Problems to be Solved by the Invention]

Extent and surface deficiency where objective of this invention controlled amount of foreign matter, hue in polyester in satisfactory level, is not former are small, also hue satisfactory molded article is to offer aromatic polyester which it can form.

Extent surface deficiency to which other objective of this invention used the aforementioned polyester, is not former is little, it means that also the hue offers satisfactory biaxially

ることにある。

[0007]

【課題を解決するための手段】

本発明の目的は、本発明によれば第一に、Sb化合物を重合触媒として重合した芳香族ポリエステルであり、極限粘度数が 0.4~1.5 の範囲にあり、該ポリエステル中の Sb 化合物の量が Sb 原子量換算で 50~400ppm であり、10 $\mu$ m 以上の大きさの異物数がポリエステル 1g 当たり 50 個以下であり、かつ Lab 法により測定されたカラーの L 値と b 値が下式(1)、(2)を満足することを特徴とする芳香族ポリエステルによって達成される。

[0008]

【数 2】

$75 \leq L - b$			(1)
$75 \leq L - b$			(1)
$b \leq 3$			(2)
$b \leq 3$			(2)

[0009]

本発明における芳香族ポリエステルのジカルボン酸成分としては、例えばテレフタル酸、ナフタレンジカルボン酸、イソフタル酸、フタル酸、ジフェニルジカルボン酸、ジフェニルエーテルジカルボン酸、ジフェニルキシエタンジカルボン酸の如き芳香族ジカルボン酸などを挙げることができる。

これらのうち、特にテレフタル酸、2,6-ナフタレンジカルボン酸が好ましく、これらはジカルボン酸成分中に占める割合が 80 モル%以上であることが好ましい。

この場合、テレフタル酸又は 2,6-ナフタレンジカルボン酸以外の前記芳香族ジカルボン酸、アジピン酸、セバシン酸の如き脂肪族ジカルボン酸、1,4-シクロヘキサジカルボン酸の如き脂環族ジカルボン酸を共重合することができる。

また、グリコール成分としては、例えばエチレングリコール、トリメチレングリコール、1,4-ブタンジオール、ジエチレングリコール、1,4-シクロヘキサジメタノール、ネオペンチレングリコール、ビスフェノール A、ビスフェノール S の如き脂肪族、脂環族、芳香族のグリコール、およびポリオキシアルキレングリコール等を挙げることができ

drawn polyester film.

[0007]

【Means to Solve the Problems】

objective of this invention, according to this invention with aromatic polyester which polymerized first, Sb compound as polymerization catalyst, limiting viscosity to be 0.4 - 1.5 ranges, quantity of Sb compound in said polyester being Sb atomic weight conversion and with 50 - 400 ppm, amount of foreign matter of size of 10 $\mu$ m or greater being polyester per gram 50 or less, At same time L value and b value of color which was measured by Lab method formula below (1), satisfy (2) are achieved with aromatic polyester which is made feature.

[0008]

【Mathematical Formula 2】

[0009]

aromatic dicarboxylic acid etc like for example terephthalic acid, naphthalenedicarboxylic acid, isophthalic acid, phthalic acid, biphenyl dicarboxylic acid, diphenylether dicarboxylic acid, diphenoxy ethane dicarboxylic acid as dicarboxylic acid component of aromatic polyester in this invention, can be listed.

Among these, especially terephthalic acid, 2,6-naphthalenedicarboxylic acid is desirable, as for these ratio which is occupied in dicarboxylic acid component is 80 mole % or more, is desirable.

In this case, terephthalic acid or 2 and 6 -naphthalenedicarboxylic acid it is possible to copolymerize cycloaliphatic dicarboxylic acid like aliphatic dicarboxylic acid, 1,4- cyclohexane dicarboxylic acid like aforementioned aromatic dicarboxylic acid, adipic acid, sebacic acid other than.

In addition, for example ethyleneglycol, trimethylene glycol, 1,4- butanediol, diethylene glycol, glycol, and polyoxyalkylene glycol etc of the aliphatic, cycloaliphatic, aromatic 1 and 4 -cyclohexane dimethanol, neopentylene glycol, bisphenol A, bisphenol S way can be listed as glycol component.

る。

これらのうち、エチレングリコール、1,4-ブタンジオールが特に好ましく、これらはグリコール成分中に占める割合が 80 モル%以上であることが好ましい。

[0010]

前記芳香族ポリエステル具体的な例としては、ポリエチレンテレフタレート、ポリブチレンテレフタレート、ポリエチレン-2,6-ナフタレート、ポリブチレン-2,6-ナフタレートを実質的な構成成分とするポリエステル、或いはこれらを主体とし、例えば前記ジカルボン酸成分および/またはグリコール成分を共重合成分とした共重合ポリエステルの挙げることができる。

[0011]

これら芳香族ポリエステルは、通常、ジカルボン酸とグリコールとをエステル化反応させる方法、ジカルボン酸ジアルキルエステルとグリコールとをエステル交換反応させる方法、またはジカルボン酸とアルキレンオキシドをエステル化反応させる方法などで、ジカルボン酸のグリコールエステルおよび/またはその低重合体を生成させ、次いでこの生成物を減圧下加熱して所定の重合度になるまで重合させることによって得られる。

上記の重合反応に使用する重合触媒には触媒能の高さ、価格面的観点から、アンチモン化合物を使用する必要がある。

このアンチモン化合物としては特に限定されず、重合触媒能を有する Sb 化合物であれば任意に使用できる。

例えば、三酸化アンチモン、四酸化アンチモン、五酸化アンチモンの如き酸化物、三塩化アンチモン、三臭化アンチモンの如きハロゲン化物、酢酸アンチモンの様なカルボン酸塩、アンチモングリコラートの如きアルコラート等が挙げられる。

中でも酸化物が好ましく、特に三酸化アンチモンが好ましい。

[0012]

前記アンチモン化合物の使用量は製造されたポリエステル中の残存アンチモン化合物量がアンチモン原子換算で 50-400ppm となるようにする必要があり、特に好ましいのは 100-350ppm である。

Among these, ethyleneglycol, 1, 4- butanediol especially is desirable, as for these ratio which is occupied in glycol component is 80 mole % or more, is desirable.

[0010]

As concrete example of aforementioned aromatic polyester, polyester, or these which designates polyethylene terephthalate, polybutylene terephthalate, polyethylene-2,6-naphthalate, polybutylene-2,6-naphthalate as effective ingredient is designated as main component, the copolyester which designates for example aforementioned dicarboxylic acid component and/or glycol component as copolymer component can be listed.

[0011]

These aromatic polyester usually, method esterification reaction of doing dicarboxylic acid and the glycol. Method transesterification of doing dicarboxylic acid dialkyl ester and glycol. Or forming, low molecular weight polymer of glycol ester and/or of dicarboxylic acid with such as dicarboxylic acid and method which alkylene oxide esterification reaction is done, under vacuum heating this product next, until it becomes predetermined degree of polymerization, it is acquired you polymerize by.

height, pricewise of catalytic ability from viewpoint, it is necessary to use the antimony compound in polymerization catalyst which is used for above-mentioned polymerization reaction.

As this antimony compound especially it cannot be limited, if it is a Sb compound which possesses polymerization catalyst talent, it can use for option.

You can list alcoholate etc like carbonate, antimony glycolate like halide compound, antimony acetate like the oxide, antimony trichloride, antimony tribromide like for example antimony trioxide, antimony tetraoxide, antimony pentoxide.

oxide is desirable even among them, especially antimony trioxide is desirable.

[0012]

As for amount used of aforementioned antimony compound remains antimony compound amount in the polyester which is produced being antimony atom conversion, it is necessary to try 50 -400 ppm ago, fact that especially it is desirable is 100 - 350 ppm.

ポリエステル中の残存アンチモン量が 50ppm 未満となると、十分な重合反応の活性が得られず、ポリエステルの製造するのに好ましくない。

一方、ポリエステルの残存アンチモン量が 400ppm を超えると、ポリマーの色相が黒ずむばかりか、アンチモン触媒残渣がポリマー中に混入し異物となる。

[0013]

熔融重合終了後はポリマーを重合槽から溶融押し出し、適当な冷媒たとえば水中で冷却し適当な大きさに切断してチップ化する。

チップは直方体でも、シリンダー状でも、サイコロ状でも球状でもよい。

また、必要に応じて固相重合を施し、所定の極限粘度数とすることも可能である。

[0014]

また、前記芳香族ポリエステルの製造に際し、必要に応じて他の添加剤、例えば整色剤、抗酸化剤、紫外線吸収剤、帯電防止剤、難燃剤等を使用してもよい。

[0015]

本発明における芳香族ポリエステルは、ポリマー 1g 中に、10 $\mu$ m 以上の大きさの異物数が 50 個以下であることが必要であり、好ましくは 30 個以下、特に好ましくは 10 個以下である。

10 $\mu$ m 以上の大きさの異物数が 50 個を超えると、例えば二軸延伸フィルムなどに成形加工する際、該異物の周辺部も延伸を受けるため異物周辺にボイド(空隙)が生じ、大きなフィルムの表面欠点を生ずる確率が高くなる。

[0016]

ポリエステル 1g 中の 10 $\mu$ m 以上の異物数を 50 個以下とする手段は特に限定されないが、例えば、前記のポリマー中に残存する Sb 化合物由来の Sb 金属量を 50~400ppm とすることは特に有効である。

[0017]

本発明における芳香族ポリエステルは、Lab 法により測定したカラー(色相)の L 値および b 値が下式(1)、(2)条件を満たす必要がある。

[0018]

When remains antimony quantity in polyester is under 50 ppm, the activity of sufficient polymerization reaction is not acquired, is not desirable in order to produce polyester.

On one hand, when remains antimony quantity in polyester exceeds 400 ppm, hue of polymer not only blackening, antimony catalyst residue mixes in polymer and becomes foreign matter.

[0013]

After melt condensation polymerization end melt extrusion it does polymer from polymerization vessel, cools at suitable coolant for example underwater and cuts off in suitable size and making into a chip does.

chip with rectangular parallelepiped and with cylinder and with dice shape and is good with spherical shape.

In addition, also it is possible to administer according to need solid phase polymerization, to make the predetermined limiting viscosity.

[0014]

In addition, it is possible to use according to need other additive, for example bluing agent, antioxidant, ultraviolet absorber, antistatic agent, flame retardant etc at the time of production of aforementioned aromatic polyester.

[0015]

As for aromatic polyester in this invention, in polymer 1g, amount of foreign matter of size of 10 $\mu$ m or greater is 50 or less, being necessary, below preferably 30, it is a particularly preferably 10 or less.

When amount of foreign matter of size of 10 $\mu$ m or greater exceeds 50, when molding and fabrication doing in for example biaxially drawn film etc, because also periphery of said foreign matter receives drawing, void (empty gap) occurs in foreign matter periphery, probability which causes surface deficiency of large film becomes high.

[0016]

means which designates amount of foreign matter of 10 $\mu$ m or greater in polyester 1g as 50 or less especially is not limited. Especially it is effective to designate Sb amount of metal of Sb compound derivation which remains in for example aforementioned polymer as 50 - 400 ppm.

[0017]

As for aromatic polyester in this invention, L value and b value of color (hue) which was measured due to Lab method formula below (1), have the necessity to fill up (2) condition.

[0018]

## 【数 3】

## [Mathematical Formula 3]

$75 \leq L - b$			(1)
$75 \leq L - b$			(1)
$b \leq 3$			(2)
$b \leq 3$			(2)

【0019】

上記式中、 $L - b$  の値は 75 以上であることが必要であるが、更に好ましくは 80 以上である。

また、 $b$  値は 3 以下であることが必要であるが、更に好ましくは 2 以下である。

$L$  値はその値が大きいほど白度良好なことを示し、 $b$  値はその値が大きくなるほど黄色味を増す。

芳香族ポリエステルが上記式の条件を満たさない場合、フィルムなどに溶融押出成形する際の熱履歴によりさらに黄着色するために、例えば包装用フィルムなどに使用する場合には色相が悪く、消費者の購買意欲を減退させてしまうため好ましくない。

芳香族ポリエステルの色相を上記式の条件となるように制御する手段は特に限定されないが、例えばポリエステル中に残存する  $Sb$  化合物触媒由来の  $Sb$  金属量を 50~400ppm とし、重合温度、重合時間を適宜調整することにより達成することができる。

【0020】

前記芳香族ポリエステルの極限粘度数は、成形加工性、加工品の強度等から、0.4 から 1.5 の範囲にあることが必要である。

【0021】

更に、本発明の第二の目的は、前記芳香族ポリエステルからなる二軸延伸フィルムによって達成される。

【0022】

この二軸延伸フィルムは、前記芳香族ポリエステルのダイから溶融押出し、冷却ドラム上で急冷して未延伸フィルムを得、ついで該未延伸フィルムを縦方向に加熱(たとえば  $T_g - 10 \sim T_g + 70$  deg C、 $T_g$ :ポリエステルのガラス転移温度)、延伸して一軸延伸フィルムとし、続いて横方向に加熱(たとえば  $T_g \sim T_g + 70$  deg C)、延伸し、さらに熱固定および/または熱弛緩することにより得る。

【0019】

In above Formula, value of  $L - b$  is 75 or greater, it is necessary, but furthermore it is a preferably 80 or greater.

In addition,  $b$  value is 3 or less, it is necessary, but furthermore it is a preferably 2 or less.

When value is large, whiteness satisfactory it shows  $L$  value,  $b$  value increases extent yellowness where that value becomes large.

When aromatic polyester condition of above Formula is not filled up, when melt extrusion molding doing in film etc, when furthermore yellow in order to color, you use for for example packaging film etc, with thermal history hue is bad, because desire to purchase of consumer it declines, is not desirable.

means which in order to become condition of above Formula, controls hue of aromatic polyester especially is not limited. It designates  $Sb$  amount of metal of  $Sb$  compound catalyst derivation which remains in the for example polyester as 50 - 400 ppm, it can achieve by suitable declaration adjusting polymerization temperature, polymerization time.

【0020】

As for limiting viscosity of aforementioned aromatic polyester, from intensity etc of molding property, processed good, from 0.4 there are 1.5 ranges, it is necessary.

【0021】

Furthermore, second objective of this invention is achieved with biaxially drawn film which consists of aforementioned aromatic polyester.

【0022】

Aforementioned aromatic polyester melt extrusion it does this biaxially drawn film, from die, quench does on cooling drum and obtains undrawn film, heating (glass transition temperature of for example  $T_g - 10 \sim T_g + 70$  deg C,  $T_g$ : polyester), draws said undrawn film next in machine direction and makes uniaxially drawn film, continuously heating (for example  $T_g \sim T_g + 70$  deg C), draws in horizontal direction, it can acquire furthermore by heat-set and/or

ことができる。

この二軸延伸フィルムの厚みは 1~300  $\mu\text{m}$ 、特に 1~150  $\mu\text{m}$  が好ましい。

この厚みが 1  $\mu\text{m}$  未満では、厚みが薄く製膜工程が安定せず極端な場合には切断に至る。

一方、この厚みが 300  $\mu\text{m}$  を超えると、過剰品質となり不経済である。

延伸倍率は、用途により異なるが縦延伸、横延伸倍率共に 2~6 倍の範囲とすることが好ましい。

延伸倍率が 2 倍未満だと、フィルムの配向が不十分で機械強度が付与されない。

一方、延伸倍率が 6 倍を超えると、延伸倍率が高すぎるため製膜が困難となるし、過剰品質となる。

また、熱固定および/または熱弛緩はフィルムの用途に合わせて、公知の手段、条件を用いることができる。

[0023]

また、本発明における二軸延伸ポリエステルフィルムには、必要に応じて易滑性を付与することが好ましい。

易滑性付与の手段は特に限定されるものではないが、例えば  $\text{SiO}_2$ 、 $\text{BaSO}_4$ 、 $\text{CaCO}_3$ 、アルミナ、アルミナシリケート、架橋有機粒子等の滑剤をポリマー中に分散させる方法や、フィルムの表面に易滑性を有する層を設ける方法などが挙げられる。

[0024]

[実施例]

以下、実施例により本発明を詳述する。

なお、実施例中「部」は、重量部を意味する。

また実施例中で用いた特性の測定法を以下に示す。

[0025]

1) 極限粘度数  $[\eta]$ : フェノール/テトラクロロエタン (重量比 60/40) の混合溶媒を用い、35 deg C で測定した溶液粘度から算出する。

[0026]

2) 色相(カラー)

thermal relaxation doing.

thickness of this biaxially drawn film 1 - 300;  $\mu\text{m}$ , especially 1 - 150;  $\mu\text{m}$  is desirable.

This thickness under 1;  $\mu\text{m}$ , thickness does not stabilize film manufacturing process thin and in extreme case reaches to cutting.

On one hand, when this thickness exceeds 300;  $\mu\text{m}$ , it becomes the excess quality and it is a uneconomic.

draw ratio differs depending upon application but both longitudinal draw, transverse draw ratio 2 - 6-fold it makes range, it is desirable.

When draw ratio 2 -fold is under, orientation of film being the insufficient, mechanical strength is not granted.

On one hand, when draw ratio exceeds 6 -fold, because draw ratio is too high, film manufacture becomes difficult and, it becomes excess quality.

In addition, heat-set and/or thermal relaxation adjusting to application of film, can use means. condition of public knowledge.

[0023]

In addition, according to need slipperiness is granted to biaxially drawn polyester film in this invention, is desirable.

means of lubricity provision is not something which especially is limited. Method of dispersing for example  $\text{SiO}_2$ ,  $\text{BaSO}_4$ ,  $\text{CaCO}_3$ , alumina, alumina silicate, crosslinked organic particle or other lubricant in polymer. You can list method etc which provides layer which possesses slipperiness in surface of film.

[0024]

[Working Example(s)]

this invention is detailed below, with Working Example.

Furthermore, "part" in Working Example means parts by weight.

In addition measurement method of characteristic which is used in Working Example is shown below.

[0025]

1) Making use of mixed solvent of limiting viscosity  $[\eta]$ : phenol/tetrachloroethane (weight ratio 60/40), it calculates from solution viscosity which was measured with 35 deg C.

[0026]

2) hue (color)

ポリマーを 140 deg C で 60 分、乾燥機中で熱処理し乾燥させた後、日本電色工業社製、色彩色差計 Z-1001DP で測定する。

[0027]

## 3) 金属量測定

蛍光 X 線(理学電気工業株式会社 蛍光 X 線 3270 型)によって所定の方法にてポリマー中の金属量(単位 ppm)を測定する。

[0028]

## 4) 異物サイズとその数

ポリマーチップ 1g をアセトン、次いでクロロホルムでその表面を良く洗浄し、ヘキサフルオロイソプロパノール(HFIP)/クロロホルム=1/1 の溶液に溶かし、目開き 1  $\mu$ m のメンブランフィルターで濾過を行い、濾取物を光学顕微鏡(200 倍)で観察し、異物の長径が 10  $\mu$ m 以上の大きさの異物の数を数える。

[0029]

## 5) フィルムの表面欠点

フィルム 1g を偏光顕微鏡で観察し、表面欠点の長径が 50  $\mu$ m を超えるものについて、以下の基準により評価する。

フィルム1gあたりの長径が50 $\mu$ mを超える異物の数が0個 .....		◎		
Quantity of foreign matter where major diameter of film per gram exceeds 50; $\mu$ m 0.....		*		
フィルム1gあたりの長径が50 $\mu$ mを超える異物の数が1～5個 .....		○		
Quantity of foreign matter where major diameter of film per gram exceeds 50; $\mu$ m 1 to 5.....		0		
フィルム1gあたりの長径が50 $\mu$ mを超える異物の数が6～10個		...		
Quantity of foreign matter where major diameter of film per gram exceeds 50; $\mu$ m 6 - 10		...		
フ	フィルム1gあたりの長径が50 $\mu$ mを超え	る異物の数が10個以上	...	×
フ	major diameter of film per gram to exceed 50; $\mu$ m	る Quantity of foreign matter 10 or greater	...	X

[0030]

## 6) フィルムの色相

フィルムを縦 10cm、横 10cm の大きさに切り出し、これを 10 枚重ねて白色の画用紙上に置く。

With 140 deg C thermal processing it does polymer in 60 min, dryer and afterdrying, measures with Nippon Denshoku Kogyo K.K. (DB 69-244-3708 ) supplied, color difference meter Z-1001DP.

[0027]

## 3) amount of metal measurement

With fluorescence X-ray (Rigaku Corp. (DB 69-054-9415 ) KK fluorescence X-ray 3270 type) amount of metal (unit ppm ) in polymer is measured with the predetermined method .

[0028]

## 4) foreign matter size and number

polymer chip 1g acetone, you wash surface next well with chloroform, meltin solution of hexafluoroisopropanol (HF IP ) /chloroform=1/1, filter with membrane filter of the mesh opening 1 ;mu m, observe filtration ones with optical microscope (200 times), major diameter of foreign matter counts quantity of foreign matter of size of 10;mu m or greater.

[0029]

## 5) surface deficiency of film

You observe film 1g with polarizing microscope, evaluation you do concerning those where major diameter of surface deficiency exceeds 50;mu m, with standard below.

[0030]

## 6) hue of film

It cuts film in size of vertical 10 cm, side 10 cm, 10 -layer repeats this and places on picture paper form of white.



これを 30 人の人が 100W の白熱灯の下で目視観察し、フィルムの色相に関し官能評価を行い、以下の基準により評価する。

This 30 people visual observation do under white incandescent lamp of 100 W, do sensory evaluation in regard to hue of film, evaluation do with standard below.

フィルムの色に黄色味あるいは黒ずみを感じる人が3人以下		...	◎
Person who feels yellowness or mildew in color of film 3 or less		...	*
フィルムの色に黄色味あるいは黒ずみを感じる人が4~6人		...	○
Person who feels yellowness or mildew in color of film 4 -6 persons		...	0
フィルムの色に黄色味あるいは黒ずみを感じる人が6~10人 ...			△
Person who feels yellowness or mildew in color of film 6 -10 persons ...			*
フ	ルムの色に黄色味あるいは黒ずみを感じる人が10人以	上	×
フ	Person who feels yellowness or mildew in color of jp11 Δ 10 persons from here	Top	X

[0031]

【実施例 1~3、比較例 1、2】テレフタル酸 3600 部とエチレングリコール 2750 部とを常温でスラリー化し、攪拌機付オートクレーブに仕込み、3kg/cm<sup>2</sup> の加圧下 270 deg C にて反応させた。

留出水量が 600 部となった時点で放圧し、更に常圧にて 270 deg C で反応させた。

さらに、製造されたポリマー中のアンチモン量が表 1 に示す量となるように、三酸化アンチモン/エチレングリコールの透明溶液を重合触媒として添加した。

引き続き重合温度 295 deg C にて徐々に高真空減圧下として 0.1mmHg で重合することにより所定のポリエチレンテレフタレートを得た。

このポリマーの品質は表 1 に示すとおりであった。

[0032]

前記ポリマーのチップを乾燥後、10 トン/日の速度で連続的に二軸ルーダーに供給し、溶融したポリマーをステンレス球焼結タイプのフィルター(ユージンカーボン社製ユージン 15G)で濾過した後、スリットより冷却したキャストイングドラム上にシート状に押し出し未延伸フィルムを得た。

続いて該未延伸フィルムを加熱ロールにて縦方向に 3.3 倍に延伸し、次いでステンターで横方向

[0031]

slurring it did [Working Example 1~3、Comparative Example 1, 2 ] terephthalic acid 3600 part and ethyleneglycol 2750 part with ambient temperature, inserted in stirrer equipped autoclave, under pressurizing 3 kg/cm<sup>2</sup> reacted with 270 deg C.

pressure release it did with time point where amount of distilled water had become 600 part, furthermore with ambient pressure reacted with 270 deg C.

Furthermore, in order to reach quantity which antimony quantity in polymer which is produced shows in Table 1, it added transparent solution of antimony trioxide/ethyleneglycol as polymerization catalyst.

Continuously predetermined polyethylene terephthalate was acquired with polymerization temperature 295 deg C by polymerizing with 0.1 mmHg as under high vacuum decompressing gradually.

quality of this polymer was as shown in Table 1.

[0032]

chip of aforementioned polymer after drying, with velocity of 10 ton /day was supplied to twin screw extruder in continuous, after filtering the polymer which is melted with filter (Eugene carbon supplied Eugene 15G ) of stainless steel ball sintering type, from slit on casting drum which was cooled extrusion undrawn film was acquired in sheet.

Consequently with heated roll in machine direction drawing said undrawn film in 3.3 times, with stentor in horizontal

に 3.6 倍に延伸して厚さ 30  $\mu$ m の二軸延伸フィルムとした。

得られた二軸延伸フィルムの表面欠点および色相の評価結果は表 2 に示すとおりであった。

[0033]

[比較例 3]三酸化アンチモン/エチレングリコールの透明溶液を重合触媒として添加した後の重合温度を 305 deg C とする以外は実施例 1 と同様を実施して所定のポリエチレンテレフタレートを得た。

このポリマーの品質は表 1 に示すとおりであった。

得られたポリマーを実施例 1 と同様にして二軸延伸フィルムに成形した。

得られた二軸延伸フィルムの表面欠点および色相の評価結果は表 2 に示すとおりであった。

[0034]

[比較例 4]三酸化アンチモン/エチレングリコールの透明溶液を重合触媒として添加した後の重合温度を 275 deg C とする以外は実施例 2 と同様を実施して所定のポリエチレンテレフタレートを得た。

このポリマーの品質は表 1 に示すとおりであった。

得られたポリマーを実施例 1 と同様にして二軸延伸フィルムに成形した。

得られた二軸延伸フィルムの表面欠点および色相の評価結果は表 2 に示すとおりであった。

[0035]

[実施例 4]三酸化アンチモンの代わり五酸化アンチモンを添加する以外は実施例 1 と同様を実施して所定のポリエチレンテレフタレートを得た。このポリマーの品質は表 1 に示すとおりであった。得られたポリマーを実施例 1 と同様にして二軸延伸フィルムに成形した。得られた二軸延伸フィルムの表面欠点および色相の評価結果は表 2 に示すとおりであった。]

[0036]

[表 1]

direction drawing next in 3.6 -fold, it made biaxially drawn film of thickness 30  $\mu$ m.

surface deficiency of biaxially drawn film which it acquires and evaluation result of hue were as shown in Table 2.

[0033]

After adding transparent solution of [Comparative Example 3] antimony trioxide/ethyleneglycol as polymerization catalyst, other than designating polymerization temperature as 305 deg C, executing in same way as the Working Example 1, it acquired predetermined polyethylene terephthalate.

quality of this polymer was as shown in Table 1.

It formed in biaxially drawn film polymer which it acquires to similar to the Working Example 1.

surface deficiency of biaxially drawn film which it acquires and evaluation result of hue were as shown in Table 2.

[0034]

After adding transparent solution of [Comparative Example 4] antimony trioxide/ethyleneglycol as polymerization catalyst, other than designating polymerization temperature as 275 deg C, executing in same way as the Working Example 2, it acquired predetermined polyethylene terephthalate.

quality of this polymer was as shown in Table 1.

It formed in biaxially drawn film polymer which it acquires to similar to the Working Example 1.

surface deficiency of biaxially drawn film which it acquires and evaluation result of hue were as shown in Table 2.

[0035]

Other than adding substituting antimony pentoxide of [Working Example 4] antimony trioxide, executing in same way as Working Example 1, it acquired predetermined polyethylene terephthalate. quality of this polymer was as shown in Table 1. It formed in biaxially drawn film polymer which it acquires to similar to the Working Example 1. surface deficiency of biaxially drawn film which it acquires and evaluation result of hue were as shown in Table 2. ]

[0036]

[Table 1]

	重合条件		ポリマー品質				
	重合温度 (℃)	重合時間 (分)	極限粘度数	Sb 金 属量 (ppm)	50 $\mu$ m 以上の 異物数	Co]-b	Co]-L-b)
実施例 1	295	165	0.642	150	9	0.5	82.3
実施例 2	295	140	0.851	380	32	1.2	79.0
実施例 3	295	180	0.640	70	6	1.8	76.4
比較例 1	295	132	0.635	420	55	3.4	73.0
比較例 2	295	—	極限粘度数 上がらず	30	3	—0.2	85.3
比較例 3	305	141	0.647	150	11	8.1	69.1
比較例 4	275	—	極限粘度数 上がらず	380	43	1.0	80.5
実施例 4	295	150	0.639	150	11	0.2	80.5

【0037】

【0037】

【表 2】

【Table 2】

	フィルム表面 欠点	フィルムの色相	総合評価
実施例 1	◎	◎	○
実施例 2	○	○	○
実施例 3	◎	○	○
比較例 1	×	△	×
比較例 3	○	×	×
実施例 4	◎	◎	○

【0038】

【0038】

表 1、2 の結果より明らかなように、本発明の芳香族ポリエステルは Sb 触媒起因の異物が非常に少なく、該ポリエステルを用いた二軸延伸ポリエステルフィルムは表面欠点が少なく、色相が良好な点で特に包装材料フィルムとして優れている。

As been clear from result of Table 1, 2, aromatic polyester of this invention the foreign matter of Sb catalytic cause is very little, biaxially drawn polyester film which uses said polyester the surface deficiency is little, it is superior in point where hue issatisfactory as especially packaging material film.

いる。

【0039】

【発明の効果】

本発明によれば、ポリエステル中の異物数、色相を良好なレベルに制御した、従来にないほど、表面欠点が少ない、色相も良好な成形加工品を成形できる芳香族ポリエステルを提供することができる。

また、該ポリエステルを使用し、従来にないほど表面欠点が少ない、色相も良好な二軸延伸ポリエステルフィルムを提供することができる。

【0039】

【Effects of the Invention】

According to this invention, extent and surface deficiency which controlled the amount of foreign matter, hue in polyester in satisfactory level, are not former aresmall, also hue satisfactory molded article can offer aromatic polyester whichit can form.

In addition, said polyester is used, extent surface deficiency which is not formeris little, also hue can offer satisfactory biaxially drawn polyester film.

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XXXXXXXXXXXXXXXXXXXXXXXXXXXX  
XXXXXXXXXXXX

【手続補正書】【提出日】

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【手続補正 1】【補正対象書類名】

明細書

specification

【補正対象項目名】

0034

0034

【補正方法】

変更

Modification

【補正内容】

【0034】【比較例 4】三酸化アンチモン/エチレングリコールの透明溶液を重合触媒として添加した後の重合温度を 275 deg C とする以外は実施例 2 と同様に実施して所定のポリエチレンテレフタレートを得た。

このポリマーの品質は表 1 に示すとおりであった。

After adding transparent solution of {0034} [Comparative Example 4] antimony trioxide/ethyleneglycol as polymerization catalyst, other than designating polymerization temperature as 275 deg C, executing in same way as the Working Example 2, it acquired predetermined polyethylene terephthalate.

quality of this polymer was as shown in Table 1.

【手続補正 2】【補正対象書類名】

明細書

specification

【補正対象項目名】

0036

0036

【補正方法】

変更

Modification

【補正内容】

JP1999152324A

1999-6-8

[0036]

[0036]

【表 1】

[Table 1]

	重合条件		ポリマー品質				
	重合温度 (℃)	重合時間 (分)	極限粘度数	S b 金 質量 (ppm)	10 μ m 以上の 異物数	Col-b	Col-(L-b)
実施例 1	295	155	0.642	150	9	0.5	82.3
実施例 2	295	140	0.661	880	32	1.2	79.0
実施例 3	295	180	0.640	70	6	1.8	76.4
比較例 1	295	132	0.685	420	55	3.4	73.0
比較例 2	295	<u>180</u>	極限粘度数 上がらず	30	3	-0.2	85.3
比較例 3	305	141	0.647	150	11	2.1	69.1
比較例 4	275	<u>140</u>	極限粘度数 上がらず	380	43	1.0	80.5
実施例 4	295	150	0.699	150	11	0.3	80.5

**Patent Number(s):** US4010145-A; DE2707832-A; **JP52105591-A**; FR2343011-A; GB1569799-A; CA1081675-A; IT1113758-B

**Title:** Polyethylene terephthalate prepn. by ester interchange - using catalyst mixt. contg. manganese, cobalt, titanium and antimony salts with phosphate ester addition prior to polycondensation

**Patent Assignee Name(s) and Code(s):** EASTMAN KODAK CO (EAST-C)

**Derwent Primary Accession Number:** 1977-18058Y [43]

**Patents Cited by Inventor:** 0

**Citing Patents:** 40

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 7

**Articles Cited by Examiner:** 0

**Abstract:**

Method comprises ester interchanging dimethyl terephthalate and ethylene glycol in the presence of a novel catalyst mixt. (I) of Mn salts in amt. of 25-110 ppm Mn, Co salts in amt. of 10-100 ppm Co, Ti alkoxide in amt. of 20-60 ppm Ti and Sb cpd. in amt. of 50-300 ppm Sb, all pts. wt. being based on the acid fraction of the polyester, prior to polycondensation.

The film and fibre forming polyester is formed at a high rate and has good colour and excellent heat-, hydrostatic- and UV stability. The novel (I), acting as catalyst-inhibitor, minimizes bathochromic shift of dye colour during dyeing or subsequent yarn of fabric treatment.

**International Patent Classification:** C08G-063/14; C08G-063/30

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds); E12 (Organometallics); F01 (Threads and fibres, natural or artificial; spinning); E11 (Containing P and/or Si); E31 (Compounds of V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Pa, V, subsequent actinides); E32 (Compounds of Ti, Zr, Hf, Cu, Ag, Au, Zn, Cd, Hg, Ga, In, Te, Ge, Sn, Pb, As, Sb, Bi)

**Derwent Manual Code(s):** A02-A06; A02-A06A; A02-A06B; A02-A06D; A02-A07A; A05-E04A; E05-J; E05-L01; E05-L02; E05-L03A; E31-M; E35-S; E35-V; F01-D04

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<b>JP52105591-A</b>	05 Sep 1977		197742		
FR2343011-A	04 Nov 1977		197751		
GB1569799-A	18 Jun 1980		198025		
CA1081675-A	15 Jul 1980		198031		
IT1113758-B	20 Jan 1986		198722		

**Application Details and Date:**

US4010145-A	US662672	01 Mar 1976
DE2707832-A	DE2707832	23 Feb 1977

**Priority Application Information and Date:**

US519953	01 Nov 1974
US576415	12 May 1975
US662672	01 Mar 1976
DE2707832	23 Feb 1977

**Patent Number(s): JP73035948-B**

**Title:** Polyester prodn - by polycondensation, in presence of nitrogen-contg cpd and strong protonic acid

**Patent Assignee Name(s) and Code(s):** TEIJIN LTD (TEIJ-C)

**Derwent Primary Accession Number:** 1973-67377U [44]

**Patents Cited by Inventor:** 0

**Citing Patents:** 0

**Articles Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Articles Cited by Examiner:** 0

**Abstract:**

Polycondensation of a bisglycol ester consisting of mainly terephthalic acid and ethylene glycol is conducted in the presence of 0.001-0.50 wt.% of an HI or HBr salt of a N-contg. cpd. (I) selected from amino-acids and amino-alcohols and a protonic acid (II) having a pKa of <5.0 at 25 degrees C respectively. (I) is e.g. glycine, alamine, tyrosine, triethylamine, ethanolamine, etc., and (II) is phosphoric acid, phosphorous acid, pyrophosphoric acid, sulphurous acid, etc. Polyester formed contains very little diethylene glycol and has excellent durability and high softening pt.

**International Patent Classification:** C08G-017/08; C08G-039/04; C08K-001/04

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

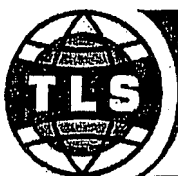
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**KOREAN / ENGLISH TRANSLATION OF**

**Korean Patent Application KR 2001 – 0089942 A**

**A Method for Manufacturing Polyester for Use in Highly Heat-Resistant Polyester Bottles**

**Your Ref: 081203 - 16**

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(54) [Title of the Invention]: **A Method for Manufacturing Polyester for Use in Highly Heat-Resistant Polyester Bottles**

**Abstract**

The invention relates to a method for manufacturing a polyester resin (PET, polyethylene terephthalate) suitable for the manufacture of polyester bottles with outstanding heat resistance that can be filled with high-temperature beverages, characterized in that, using purified terephthalic acid (TPA) and ethylene glycol (EG) as the main raw materials, catalysts, cocatalysts, and thermal stabilizers are mixed in appropriate concentrations to manufacture a base chip having intrinsic viscosity (IV) in the range of 0.55 to 0.67 dL/g, and the chip is then crystallized and subjected to solid-state polymerization to obtain a heat-resistant resin showing high viscosity of 0.70 to 1.0 dL/g.

The highly heat-resistant resin of the invention can be used for the molding of high-transparency bottles having particularly outstanding characteristics with respect to heat deformation, crystallization, and shrinkage during high-temperature filling of fruit beverage bottles with liquids ranging from 85 to 105°C.

In particular, the invention provides a polyester resin that can be molded into a high-transparency bottle that can be used for the filling of beverages in a temperature range of 90 to 95°C, considerably higher than the range for conventional heat-resistant bottles (filling temperature 85 to 88°C).

### *Specification*

#### *Detailed Description of the Invention*

##### *Purpose of the Invention*

##### *Technological Field of the Invention and Prior Art*

The invention relates to a method for manufacturing a polyester resin suitable for the manufacture of polyester bottles with outstanding heat resistance that can be filled with high-temperature beverages.

Initially, PET (polyethylene terephthalate) was used mainly in the field of textiles as a thermoplastic polyester resin manufactured by reacting purified terephthalic acid (TPA) and dimethyl terephthalate (DMT) with ethylene glycol (EG), but it is currently used in the molding of biaxially-oriented stretch-blown bottles, which are widely used in applications such as containers for bottled water, carbonated beverages, alcoholic beverages, fruit juice drinks, and wrapping of general food products.

In particular, PET containers show outstanding mechanical properties, gas barrier properties, chemical resistance, transparency, and luster, and their use is expected to increase considerably in the future.

The majority of PET containers are used for filling of contents at room temperature or temperatures of 70°C and above, while filling of fruit juice beverages is carried out at temperatures of 85 to 88°C. High-temperature filling is carried out in order to meet the requirements of sterilization, bleaching, and prevention of oxidation.

When molded containers made of such existing PET resins are sterilized by hot-water washing, they tend to undergo deformation, so it has been difficult to use them as containers for high-temperature sterile filling.

### *Technical Problems to be Solved by the Invention*

In manufacturing the polyester resin (PET) of the invention, which has a highly transparent, high-viscosity, highly heat-resistant linear polymer structure, by selecting and mixing the additives to be used at the melt polymerization stage, one can optimize the manufacturing conditions for clean polymers and the molding conditions for heat-resistant bottles, thus providing a method for manufacturing a polyester resin and molding bottles made of said resin that makes it possible to produce highly heat-resistant containers in which the beverage filling temperature can be increased from the existing level of 85 to 88°C to a level of 92 to 100°C.

In the polyester manufacturing method of the invention, terephthalic acid and dimethyl terephthalate (DMT) are mixed with ethylene glycol and subjected to polyester polymerization in order to obtain a polyester resin having a linear polymer structure, thus obtaining a highly heat-resistant polyester resin that makes it possible to keep the container shrinkage ratio at 1.5 or less during high-temperature liquid filling at temperatures of 90°C or above.

The bottle molding method according to the invention makes it possible to manufacture PET resin having the physical properties of intrinsic viscosity of 0.5 to 1.0 and a melting point of 245 to 260°C. By means of a process in which the preform is molded at a temperature of 275 to 295°C, crystallization of the neck portion is carried out at 100 to 200°C, heat-setting is carried out at 160 to 200°C, and multistage blowing is carried out at a temperature of 90 to 120°C and a pressure of 20 to 40 kg/cm<sup>2</sup>, one obtains a container suitable for the filling of high-temperature liquids at 90°C or above.

### *Composition and Operation of the Invention*

The following is a detailed explanation of the polyester resin manufacturing method and bottle molding method of the invention.

In the invention, high-purity terephthalic acid (TPA) and ethylene glycol (EG) are used as raw materials, and catalysts, thermal stabilizers, cocatalysts, color-improving agents, etc., are mixed in at specified concentrations to obtain a base polymer having an intrinsic viscosity (IV) of 0.550 to 0.670 dL/g, after which crystallization and solid-state polymerization are carried out to manufacture a high-viscosity resin having an intrinsic viscosity (IV) of 0.70 to 1.0 dL/g, thus providing a process for molding bottles used for the filling of high-temperature beverages.

PET is prepared as a base polymer having a degree of polymerization of approximately 100 by carrying out esterification and polycondensation using terephthalic acid (TPA) and

ethylene glycol as the main raw materials, and this base polymer is then subjected to crystallization and solid-state polymerization in order to obtain a high-viscosity polymer (having an intrinsic viscosity of 0.70 to 1.0 dL/g).

Substances such as high-purity isophthalic acid, phthalic acid, 1,4-cyclohexane dimethanol, diethylene glycol, and bisphenol derivatives may be used as the main raw materials.

Important physical properties of the resin include intrinsic viscosity (IV), color, melting point, carboxy end groups, diethylene glycol (DEG) content, etc.

Concerning pellet size, in order to make the degree of crystallization and the melting point uniform after polymerization, it is preferable to manufacture the base polymer under as sterile conditions as possible beginning from the manufacturing stage, with pellets ordinarily being manufactured in a weight range of 1.5 to 3.0 g per 100 pellets.

As problems such as non-uniform physical properties or unstable material flow may occur during the solid-state polymerization process when pellets are made in excessively small powder form in order to increase their relative surface area, the particular characteristics of the equipment used should also be borne in mind.

Antimony trioxide and antimony triacetate are used as polymerization catalysts, with a mixing ratio of the two substances of 0 : 1,000 to 50 : 50, and the catalyst used must be high-purity catalyst (purity of 99.80%) virtually free of insoluble impurities such as  $Sb_nO_m$  ( $n = 2$ ,  $m = 3$  to 5) and metallic components such as Pb and N.

Moreover, in order to impart thermal stability during postprocessing, phosphorus compounds may be mixed in and used together with ethylene glycol in manufacturing, and in order to improve resin color, cobalt acetate and tin compounds may be used in specified concentrations as cocatalysts.

Catalysts, cocatalysts, heat stabilizers, etc., may be added immediately before esterification or polycondensation, completely dissolving and dispersing them in the ethylene glycol, after which precision filtering is carried out using a 1 to 2  $\mu$  filter.

In particular, in order to achieve a uniform melting point and stabilize molecular structure, it is extremely important to maintain a uniform concentration and a stable quantitative supply of such submaterials.

Antimony trioxide, antimony triacetate, and germanium oxide may be used as polycondensation catalysts either alone or in combination in concentrations of 200 to 750 ppm/PET, phosphorus compounds may be used as thermal stabilizers in concentrations of 100 to 200 ppm/PET, and cobalt acetate in a concentration of 50 to 200 ppm and tin compounds in a concentration of 10 to 100 ppm may be used as cocatalysts. Phosphates such as trimethyl phosphate, triethyl phosphate, and triphenyl phosphate may be used as phosphorus compounds.

In the esterification stage, the reaction is carried out at a pressure of approximately  $1.0 \text{ kg/cm}^2$  and a temperature in the range of  $245$  to  $260^\circ\text{C}$  to obtain an oligomer having a degree of polymerization of 3 to 10, after which, in the polycondensation stage, the reaction is carried out at  $275$  to  $285^\circ\text{C}$  under a high vacuum with a pressure of 1 torr or less to manufacture a melt polymer with an intrinsic viscosity of  $0.57$  to  $0.67 \text{ dL/g}$  and a standard pellet weight of 1.5 to 3.0 g/100 pellets.

The basic pellets, which have a super bright, fully transparent linear polymer structure, are subjected to the various phases of precrystallization, crystallization, and solid-state polymerization in order to manufacture a high-viscosity resin having a degree of crystallization of 45 to 60 and an intrinsic viscosity of  $0.70$  to  $1.0 \text{ dL/g}$ .

This solid-state resin has a melting point ranging from  $245$  to  $260^\circ\text{C}$ , and it is therefore used not only as a material for bottles filled with high-temperature beverages but also in ordinary pressurized and non-pressurized containers.

PET has a glass transition temperature ( $T_g$ ) of  $67$  to  $81^\circ\text{C}$ , and the temperature at which deformation begins to occur is approximately  $70^\circ\text{C}$ . It has been confirmed that if high heat resistance is imparted from the resin manufacturing stage and appropriate heat setting is carried out in the container molding process, it is possible to manufacture stable, heat-resistant PET containers for hot filling with beverages at much higher temperatures than the range of  $85$  to  $88^\circ\text{C}$  possible with conventional containers.

This heat-resistant PET resin is manufactured with an intrinsic viscosity of  $0.70$  to  $1.10 \text{ dL/g}$ , it is then dried to reduce its water content to 50 ppm, and it is molded into a bottle using the molding machine described below. The bottle-molding method of the invention is described in the following.

- 1. Drying of PET pellets**

The pellets are dried for 3 to 6 hours at a temperature of  $140$  to  $180^\circ\text{C}$  so as to reduce their water content to 50 ppm or below.

- 2. Molding of preform**

The preform is molded at  $270$  to  $295^\circ\text{C}$ .

- 3. Crystallization of neck component**

The neck component is crystallized by cooling from a temperature of  $100$  to  $125^\circ\text{C}$  for 200 to 400 sec with water chilled to a temperature of  $10$  to  $30^\circ\text{C}$ .

- 4. Heat setting and blowing**

Primary blowing is first carried out at  $15$  to  $30 \text{ kg/cm}^2$  and  $80$  to  $140^\circ\text{C}$ .

The heat-setting temperature is set at  $160$  to  $190^\circ\text{C}$ .

Secondary blowing is carried out at  $20$  to  $45 \text{ kg/cm}^2$  and  $80$  to  $130^\circ\text{C}$ .

## 5. Testing and packaging

External appearance and transparency tests, heat resistance tests (testing of shrinkage 5 minutes after filling with hot water at 92°C).

In order to mold a high-temperature beverage container from pellets obtained by high-viscosity solid-state polymerization, the pellets must be dried to a water content of 50 ppm or less. The preform is manufactured under injection molder barrel temperature conditions of 270 to 295°C, after which the mouth portion of the preform (bottle mouth) is crystallized at 100 to 125°C, cooled, and then sent to the blowing unit.

The mouth of the bottle is crystallized because it is the first part to come into contact with the high-temperature beverage during filling. In the process of molding the mouth component, the crystallized preform is heated in the blowing device to 80 to 140°C and subjected to primary blowing with compressed air at a pressure of 50 to 30 kg/cm<sup>2</sup>, after which the temperature is increased to 160 to 190°C, heat setting is carried out, and secondary blowing is carried out using compressed air at a temperature of 80 to 130°C and a pressure of 20 to 45 kg/cm<sup>2</sup>, thus manufacturing the completed molded form into a heat-resistant bottle.

During the testing process, testing of the external appearance of the bottle is carried out, including properties such as heat resistance, uniformity of drawing, specimen thickness, and bottom gate center properties, and in order to measure heat resistance, the bottle is filled with hot water at a temperature of approximately 92°C and left standing for a period of 5 min. or longer, the volume before and after filling with hot water is measured, and the shrinkage rate is determined.

Although there are differences among the standards used at various bottle manufacturing companies, a tolerance has been adopted of a change in shrinkage rate of 1.5 or less in testing with hot water at 92°C.

### [Working Examples]

Antimony acetate in the amount of 500 to 700 ppm/PET, cobalt acetate in the amount of 100 to 150 ppm/PET, triethyl phosphate in the amount of 150 to 200 ppm, and a tin compound in the amount of 10 to 50 ppm were added to high-purity terephthalic acid (TPA) and ethylene glycol (EG) to manufacture a resin (polymer), which was then subjected to solid-state polymerization up to an intrinsic viscosity of 0.85 to manufacture a 1.5 L juice container.

**Table 1. Physical properties of melt polymer (base polymer) and solid-state polymer**

Classification	Intrinsic viscosity (IV)	Color		Carboxyl end group (Eq/TON)	Melting point (°C)	Acetaldehyde (ppm)	DEG content (wt)	100EA weight (g)	Bottle shrinkage after molding ( )
		L	b						
Base polymer	0.654	51.2	-0.46	18.6	255.8	55.0	1.21	2.5	0.6
Solid-state polymer	0.851	89.0	2.3	2.3	252.8	0.30	1.15	2.5	

\* The melt polymer was manufactured by batch polymerization, and the solid-state polymer was manufactured using a continuous-type unit.

**Table 2. Molding conditions of heat-resistant bottle**

		Molding step		Production conditions		
Pellet drying			160°C x 4 h			
Injection molder barrel temperature (preform manufacturing)		Neck	Front		Rear	
			280°C	280°C	280°C	
		Crystallization of neck component		110°C x 300 sec		
		Primary blowing		25 kg/cm <sup>2</sup> x 170°C		
		Heat setting		180°C x 6 sec		
		Secondary blowing		350 kg/cm <sup>2</sup> x (100-104°C)		
		Chilled water		15°C Chilled Water		
Molded bottle		Volume		1.5 L Juice bottle		
			Transparency		Haze 0.3 or below (favorable)	
					Favorable	
					Shrinkage 0.6 (92°C hot water)	

As shown in Tables 1 and 2 above, by molding a heat-resistant bottle using resin manufactured by the method of the invention, it was possible to obtain a bottle allowing filling of a beverage at 92 to 100°C, a much higher temperature than bottles currently on the market, and hot-water-induced shrinkage was also confirmed to be outstanding, with a value of 1.



### *Effect of the Invention*

In contrast to conventional molded fruit drink bottles, which ordinarily can be filled with hot beverages at temperatures of 85 to 88°C, the invention provides a polyester resin that allows manufacturing of a heat-resistant bottle that has raw materials with improved internal density, allows filling temperatures over a broad range, does not show deformation at temperatures of 90 to 95°C, and shows a broad range of thermal resistance over a range of 85 to 100°C.

### *(57) Claims*

#### **Claim 1**

A method for manufacturing a polyester resin having a linear polymer structure by polyester polymerization of dimethyl terephthalic acid and dimethyl terephthalate (DMT) with ethylene glycol, characterized in that said polyester resin can be used to manufacture heat-resistant bottles that allow filling of high-temperature liquids at temperatures of 90°C or above and show container volume shrinkage of 1.5 or less.

#### **Claim 2**

The method for manufacturing a polyester resin for use in heat-resistant containers according to Claim 1,

characterized in that antimony trioxide, antimony triacetate, or germanium oxide are added alone or in combination in amounts of 200 to 750 ppm/PET as polycondensation catalysts, a phosphorus compound is added in the amount of 100 to 200 ppm/PET as a heat stabilizer, and cobalt acetate in the amount of 50 to 200 ppm or a tin compound in the amount of 10 to 100 ppm are added as cocatalysts.

#### **Claim 3**

The method for manufacturing a polyester resin according to Claim 2,

characterized in that the above phosphorus compound is trimethyl phosphate, triethyl phosphate, or triphenyl phosphate.

#### Claim 4

The method for manufacturing a polyester resin for use in a heat-resistant fruit juice beverage container according to Claims 1 or 2,

characterized in that high-purity isophthalate, phthalic acid, 1,4-cyclohexane dimethanol, diethylene glycol, or bisphenyl derivatives are used as additives.

#### Claim 5

The method for manufacturing a container for high-temperature filling at 90° or above according to Claims 1 or 2,

characterized in that, in manufacturing of a PET resin having the physical properties of intrinsic viscosity of 0.5 to 1.0 and a melting point of 245 to 260°C, a preform is molded at 275 to 295°C, a neck component is subjected to crystallization at 100 to 200°C, heat setting is carried out at 160 to 200°C, and multistage blowing is carried out at a temperature of 90 to 120°C and a pressure of 20 to 40 kg/cm<sup>2</sup>.



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### **KOREAN / ENGLISH TRANSLATION OF**

**Korean Patent Application KR 1997 - 0007952 B 1**

**A Method for Manufacturing a Polyester Resin for Use in Food Containers**

**Your Ref: 081203 - 12**

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(54) [Title of the Invention]:	<b>A Method for Manufacturing a Polyester Resin for Use in Food Containers</b>
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**Abstract**

No abstract.

**Specification**

[Title of the Invention]

A method for manufacturing a polyester resin for use in food containers.

[Detailed Description of the Invention]

The invention relates to a method for manufacturing a polyester resin for use in food containers, and more specifically, an economical method for the manufacture, without using solid-state polymerization, of a polyester resin suitable for use in containers for carbonated beverages, bottled water, and fruit drinks, etc., in which, during manufacturing of the polyester polymer, an inert gas is blown into the melt to form prepolymer pellets containing air bubbles,

said pellets are heated, and a vacuum is simultaneously applied in order to manufacture polymer pellets, after which crystallization and drying are carried out.

There is currently a dramatic increasing trend in the demand for polyester resins for use in food containers, and in order to meet this demand, melt polymerization followed by solid-state polymerization has conventionally been used in manufacturing these polyester resins, particularly polyethylene terephthalate (abbreviated in the following as PET), in order to impart various physical properties to the resin.

In manufacturing of PET in particular, the advantages of solid-state polymerization of polyester resins include increased strength due to the formation of high-molecular-weight compounds and the elimination of acetaldehyde, which adversely affects the taste of food. With the recent development of melt polymerization methods, it has become possible to easily obtain polymers having a sufficient molecular weight for use in containers by means of processes in which melt polymerization is used, without the solid-state polymerization process, but it has not yet been possible to solve the problem of impaired taste.

The inventors of the invention therefore conducted research on methods for economically manufacturing polyester resins for use in food containers without carrying out solid-state polymerization, developing a process in which an inert gas is blown in during the melt polymerization process in order to manufacture polymer pellets that are then crystallized and dried, thus arriving at the invention.

The object of the invention is to provide a new method for manufacturing polyester resin for use in food containers without using the solid-state polymerization process.

The following is a detailed description of the invention.

The invention relates to a method for manufacturing a polyester resin for use in food containers in which, during manufacturing of the polyester polymer, an inert gas is blown into the melt to form polyester prepolymer pellets containing air bubbles, said pellets are heated under a vacuum to obtain popcorn-type polymer pellets, after which crystallization and drying are carried out.

The following is an explanation of the invention in greater detail.

The invention relates to a process in which a polyester resin for use in food containers is manufactured by means of the method of blowing an inert gas into the melt polymer during the melt polymerization process. During this process, the inert gas is blown in from the bottom of the polymerization reactor during melt polymerization in order to form polyester prepolymer pellets containing air bubbles, the pellets are crystallized by increasing the temperature from room temperature under a vacuum, causing the pellet-shaped chips to break up and take on the appearance of popcorn, these popcorn-like polyester polymers are crystallized, and acetaldehyde is removed.

The melt polymerization of the polyester of the invention is carried out according to a method commonly known to the one skilled in the art, and the reaction temperature, catalysts, catalyst content, and stabilizers used are all well-known in the literature and in the field of polyester prepolymer manufacturing.

The polyester prepolymer used in the invention is a commonly-known polymer mainly containing PET or 80 mol % or more of ethylene terephthalate structural units, and polyesters allowing solid-state polymerization, such as polyethylene isophthalate, polycyclohexane diethylterephthalate, and polyethylene naphthalate may also be used.

Moreover, the polyester prepolymer may also contain dicarboxylic acids or ester compounds thereof such as isophthalic acid, dimethylisophthalate, orthophthalic acid, diethylorthophthalate, naphthalene dicarboxylic acid, or dimethyl naphthalene dicarboxylate and polymer compounds such as 1,4-butane diol, neopentyl glycol, 1,4-cyclohexane dimethanol, and propylene glycol.

The polyester prepolymer pellets used in the invention are manufactured by blowing an inert gas into the polymer melt in order to carry out pelletization, with this process being carried out from 60 minutes prior to completion of the polycondensation until the reaction is completed, or more preferably, until the completion of polycondensation.

In this case, an inert gas such as nitrogen, argon, helium, or neon may be used, with nitrogen being the preferred substance. The volume of the inert gas blown in should be 0.1 to 5,000%, and preferably 0.5 to 300%, with respect to the volume of the polymer melt. An extrusion die for direct blowing and distribution of the inert gas may be installed for blowing the inert gas into the polyester prepolymer.

The polyester pellets containing the inert gas used in manufacturing according to the above method are then placed under a vacuum during the crystallization stage, thus molding them into chips having the appearance of popcorn. The degree of vacuum used is 10 torr or less.

In this case, if the above vacuum is greater than 10 torr, it will take too long to form the popcorn-shaped chips, producing an unfavorable result. A suitable temperature range is 75 to 230°C, and preferably 100 to 180°C. If the temperature is too low, the popcorn chips will not be formed, and if it is too high, although crystallization will take place, the formation of the popcorn-shaped chips will not occur.

It is important to note that the bubbles in the prepolymer must have popped before crystallization takes place. If crystallization is carried out before the bubbles inside the prepolymer have popped, it will have a shape identical with that of ordinary polyester prepolymers, and the popcorn-shaped chips will not form.

In manufacturing of the popcorn-shaped polyester resin by the above method, these polyester pellets will typically be heated for 5 to 300 minutes at 120 to 180°C and crystallized

with a target degree of crystallization of 20% or more. Adhesion of the polyester pellets is prevented in the drying process.

A dehumidifying dryer can be used to decrease the acetaldehyde content of the popcorn-shaped polyester resin crystallized as described above. In carrying out drying to remove acetaldehyde, the temperature is increased to 160 to 200°C, and the polyester resin is then passed through the dehumidifying dryer for 2 to 20 hours, and preferably 3 to 10 hours, making it possible to decrease its acetaldehyde content to 1 ppm or below. If the above drying, for the purpose of the removal of the acetaldehyde, is carried out at 160° or below, the acetaldehyde-removing effect will be small, and if the temperature exceeds 200°C, the color of the polyester resin will change and thermal decomposition and oxidative decomposition will occur. Moreover, the dew point of the dehumidified air used in this case should be -20°C or below, and preferably -40°C or below, and the volume used should be 0.05 to 1,000 L per kg of the polyester resin.

In addition to dehumidified air, the above acetaldehyde removal process may also be carried out using a vacuum or inert gas, with suitable inert gases including nitrogen, carbon dioxide, helium, argon, and neon. The intrinsic viscosity of the polyester resin according to the invention should be in the range of 0.6 to 1.3 dL/g in order to maintain the physical properties of the container.

Using the method of the invention, a polyester resin for use in food containers can be manufactured by an economical method that does not require the use of solid-state polymerization. In addition to polyester resin, the method can also be used for the removal of impurities such as volatile substances from all resins.

The following is an explanation of the invention in further detail by means of working examples, but the invention is by no means limited by these examples.

In Working Examples 1-6 and Comparison Examples 1-3 below, the intrinsic viscosity of the manufactured PET polymer pellets and PET resin was measured at 30°C using a mixed solvent composed of phenol/tetrachloroethane (in a ratio 6 : 4 by weight). Furthermore, in order to measure the acetaldehyde content of the PET polymer pellets and PET resin, 5 g of PET pellets or PET resin was frozen using liquid nitrogen and pulverized, 1.0 g of the pulverized sample was placed in a tube and heated for 10 minutes at 160°C, a 5 mL sample was removed from the tube, and this sample was measured by gas chromatography.

### **Working Example 1**

5 minutes prior to the completion of the polycondensation of polyethylene terephthalate (PET) polymer, 5 vol. % of nitrogen with respect to the volume of PET polymer was injected via the bottom of the reactor, the mixture was stirred, and extrusion and cutting were carried out to



obtain round pellets measuring 3 x 3 x 2 mm. The intrinsic viscosity of the PET polymer pellets was 0.75 dL/g, and their acetaldehyde content was 46 ppm.

50 g of prepolymer chips containing round bubbles were placed in a rotatory vacuum distiller and heated under a vacuum at 120°C for 30 minutes. In order to convert the PET polymer pellets into a popcorn shape, the temperature was continuously increased to 140°C and crystallization was carried out for 60 minutes.

After this, in order to remove the acetaldehyde, the vacuum was released, the temperature was increased to 170°C, and air with a dew point of -42°C was passed through zeolite at a rate of 50 mL per minute for 4 hours. The acetaldehyde content of PET resin subjected to the above process was 1.3 ppm.

#### **Working Example 2**

The same method as in Working Example 1 was used, except that the temperature for the acetaldehyde removal was set at 170 to 180°C. The acetaldehyde content of PET resin subjected to this process was 0.9 ppm.

#### **Working Example 3**

The same method as in Working Example 1 was used, except that the temperature for the acetaldehyde removal was set at 170 to 180°C. The acetaldehyde content of PET resin subjected to this process was 0.8 ppm.

#### **Working Example 4**

The same method as in Working Example 1 was used, except that during drying, for the purpose of the removal of the acetaldehyde, the dehumidified air was passed through for 6 hours rather than 4 hours. The acetaldehyde content of PET resin subjected to this process was 1.0 ppm.

#### **Working Example 5**

The same method as in Working Example 2 was used, except that during drying, for the purpose of the removal of the acetaldehyde, the dehumidified air was passed through for 6 hours rather than 4 hours. The acetaldehyde content of PET resin subjected to this process was 0.8 ppm.

### **Working Example 6**

The same method as in Working Example 3 was used, except that during drying, for the purpose of the removal of the acetaldehyde, the dehumidified air was passed through for 6 hours rather than 4 hours. The acetaldehyde content of PET resin subjected to this process was 0.5 ppm.

### **Comparison Example 1**

PET resin pellets were manufactured by means of the usual method without injecting inert gases during polycondensation of the PET polymer. The intrinsic viscosity of the PET was 0.76 dL/g. These PET resin pellets were placed in the same rotatory vacuum distiller used in Working Example 1, and while heating to 120°C, crystallization was carried out for 30 minutes under a vacuum. After this, the vacuum was released, the temperature was increased to 170°C, and air having a dew point of -42°C was passed through at a rate of 50 mL per minute for 4 hours. The acetaldehyde content of PET subjected to this process was 1.85 ppm.

### **Comparison Example 2**

The same method as in Comparison Example 1 was used, except that the temperature during acetaldehyde removal was set at 170 to 180°C. The acetaldehyde content of PET resin subjected to this process was 14.1 ppm.

### **Comparison Example 3**

The same method as in Comparison Example 1 was used, except that the temperature during acetaldehyde removal was set at 170 to 180°C. The acetaldehyde content of PET resin subjected to this process was 11.3 ppm.

## **(57) Claims**

### **Claim 1**

A method for manufacturing a polyester resin for use in food containers, characterized in that, in the process of manufacturing the polyester polymer, an inert gas is blown into the polymer melt to form polyester prepolymer pellets containing air bubbles, and while these are heated at 100-180°C, a vacuum of 10 torr or less is applied to form the polymer pellets into a popcorn shape, after which crystallization and drying are carried out.

**Claim 2**

The method for manufacturing a polyester resin for use in food containers according to Claim 1, characterized in that the aforementioned polyester prepolymer contains polyethylene terephthalate or 80 mol % or more of ethylene terephthalate structural units.

**Claim 3**

The method for manufacturing a polyester resin for use in food containers according to Claim 1, characterized in that the above drying is carried out at a temperature of 160-200°C.

**Patent Number(s):** NL7113206-A; DE2147835-A; FR2108010-A; US3796691-A; JP74020078-B; GB1364732-A; DE2147835-B

**Title:** Linear polyesters prodn - by polycondensation of glycol terephthalate in presence of antimony, tin and phosphorus cpds

**Patent Assignee Name(s) and Code(s):** MITSUBISHI RAYON CO LTD (MITR-C); (MITR-C)

**Derwent Primary Accession Number:** 1972-23408T [15]

**Patents Cited by Inventor:** 0

**Patents Cited by Examiner:** 0

**Citing Patents:** 8

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**Articles Cited by Examiner:** 0

**Abstract:**

Linear polyesters with improved whiteness and transparency are made by polycondensation of glycol terephthalates in the presence of (1) a trivalent Sb cpd (2) a P cpd. and (3) an organotin cpd., where the (1), (2) and (3) are compatible with the polycondensation system and the ratio Sn/Sb is  $\geq 0.2$  (esp. 0.3-4) and the ratio P/Sn is  $\geq 1$  (esp. 1.5-10). The Sb cpd. is pref. Sb<sub>2</sub>O<sub>3</sub>. Suitable Sn cpds. have 2-24C and at least one Sn-C bond.

**International Patent Classification:** B01J-011/00; C08G-017/15; C08G-063/34; D01F-007/04

**Derwent Class:** A23 (Polyamides, polyesters, polycarbonates, alkyds)

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**WO 01/14452 A1**

(54) Title: PREPARATION OF POLYESTERS EMPLOYING ANTIMONY CATALYSTS AND ACIDIC PHOSPHORUS COMPOUNDS

(57) Abstract: The process for the production of polyesters, and in particular polyethylene terephthalate (PET) involves polymerization, e.g., polycondensation, of one or more diacids and one or more diols in the presence of both an antimony catalyst and an acidic phosphorus-containing additive like e.g. phosphoric acid. The acidic phosphorus additive is introduced prior to the antimony catalyst, preferably by an amount of time to allow a reaction between the additive and at least one diol of the (s) present in the reaction mixture. A polyester resin produced by this process is also provided.

PREPARATION OF POLYESTERS EMPLOYING ANTIMONY CATALYSTS AND ACIDIC  
PHOSPHORUS COMPOUNDS

5

**RELATED APPLICATION**

This application is related to International Application [Needle & Rosenberg  
Docket No. 05015.0233/P] filed concurrently herewith, which is incorporated herein  
10 by reference in its entirety.

**FIELD OF THE INVENTION**

The present invention relates to processes for producing polyester resins and in  
15 particular poly(ethylene) terephthalate (PET) containing low levels of phosphorus  
containing additives that is suitable for use in a variety of applications including the  
manufacture of articles such as containers.

**BACKGROUND OF THE INVENTION**

20

It is well known in the art that polyesters such as poly(ethylene terephthalate)  
(PET) are useful for many packaging applications. In fact, PET or modified PET is a  
polymer of choice for making beverage and food containers, particularly carbonated  
beverage containers.

25

Poly(ethylene terephthalate) may be derived from multistep processes well  
known in the art which may include the direct esterification of ethylene glycol and  
terephthalic acid. In addition, it is known that PET can be modified with additional  
acidic and/or glycol comonomers, e.g., isophthalic acid (or dimethyl isophthalate),  
30 1,4-cyclohexanedimethanol (CHDM), and the like. Modifying PET with additional  
comonomers may improve some of the physical properties of the resulting polyesters

and provide particularly desired properties in an article formed from the polyester particularly in the areas of crystallization and processability.

5        Polyesters such as PET are typically formed via three-stage processes. The three preferred stages are often referred to as the esterification stage, the prepolymer stage, and the polycondensation stage.

10        Each of the stages can employ catalysts and certain additives. For example, since both the prepolymer stage and the polycondensation stage employ the same basic reaction, a variety of polycondensation catalyst systems are recognized in connection with the prepolymer and polycondensation stages. Examples of such catalysts includes titanium, gallium, germanium, tin, and antimony compounds. The use of additives is also known in the art. Additives that are recognized in the art include phosphorus-containing stabilizers such as phosphates and phosphoric acid. In 15        this regard, such phosphorus-containing additives are considered interchangeable.

As background in this regard, attention is directed towards the following patents that discuss the use of phosphorus-containing additives:

20        U.S. Patent 4,499,226, issued Feb. 12, 1985, and assigned to Goodyear Tire & Rubber Company, discloses process for producing high clarity colorless polyesters which include the use of polycondensation catalysts, cobalt-containing compounds and phosphorus-containing additives.

25        German Patent Application 195 37 930 A1, opened to public inspection on April 17, 1997, and assigned to Zimmer, AG, also discloses a continuous process for the production of transparent polyesters in which unpurified diol that has been eliminated during the polycondensation stage can be internally recycled into the process.

U.S. Patent 4,110,316, issued Aug. 29, 1978 and assigned to E.I. Du Pont de Nemours and Company, discloses a process for producing fiber-forming polyester from ethylene glycol and terephthalic acid that includes the use of color inhibitors such as phosphoric acid and triphenyl phosphite.

5

U.S. Patent 5,243,022, issued Sept. 7, 1993 and assigned to Korea Institute of Science and Technology, discloses a method for forming polyesters that involves forming prepolymers from a first portion of esterification product in the presence of certain catalysts and stabilizers. The prepolymers are then polycondensed together  
10 with a second portion of esterification product to form the polyester.

U.S. Patent 5,235,027, issued Aug. 10, 1993 and assigned to Zimmer Aktiengesellschaft, discloses a process for making a modified copolyethylene terephthalate that includes the addition of a phosphorus-oxygen compound before  
15 polycondensation in an amount that corresponds to a Sb: P weight ratio of at least four.

However, careful consideration of the art reveals serious errors, inconsistencies and contradictions in the way the art views phosphorus-containing  
20 additives, particularly the use of low levels of acidic additives in polyester formation.



## SUMMARY OF THE INVENTION

The present invention is based, in part, on the surprising discovery that the  
5 choice of phosphorus-containing additive, when employed in connection with certain  
polymerization catalysts, can have a significant impact on reaction rate of the  
polymerization process as well as the clarity of the resulting polyester. Further, it was  
surprisingly found that the optimal relative addition sequence of the catalyst and  
phosphorus-containing additive was impacted by the both choice and level of  
10 phosphorus-containing additive.

One aspect of the present invention involves a process for making a polyester  
resin including the steps of:

- 15 (a) esterifying at least one dicarboxylic acid component and at least one  
diol component; and
- (b) polymerizing the product of step (a) under conditions effective to  
provide a polyester resin,

wherein the polymerization step (b) occurs in the presence of (i) an antimony-based  
polymerization catalyst and (ii) an acidic phosphorus-containing additive, with the  
20 additive (ii) being added prior to the catalyst (i) so as to provide a polyester resin that  
is at least substantially free of inorganic compounds formed from a reaction of the  
catalyst (i) and additive (ii). The amount of additive is preferably not greater than  
about 45 ppm based on elemental phosphorus in the resulting polyester.

25 In addition the process can include a prepolymer stage between steps (a) and  
(b). The process can further include additional step such as solid-phase  
polymerization of the polyester resin from step (b). Moreover, the polymerization step  
(b) is preferably performed in the absence of added cobalt compound(s).

Another aspect of the present invention relates to a process that includes (a) esterifying at least one dicarboxylic acid component and at least one diol component; and

polymerizing the product of step (a) under conditions effective to provide a polyester resin, wherein the polymerization step (b) occurs in the presence of (i) an antimony-based polymerization catalyst and (ii) an acidic phosphorus-containing additive, with the catalyst (i) being added after, the additive (ii), and the acidic phosphorus containing additive (ii) is added sufficiently before the polycondensation catalyst (i) such that the additive (ii) can react with the at least one diol.

10

Yet another aspect of the present invention include process for making polyester resin that includes (a) esterifying at least one dicarboxylic acid component and at least one diol component; and (b) polymerizing the product of step (a) under conditions effective to provide a polyester resin, wherein the polymerization step (b) occurs in the presence of (i) an antimony-based polymerization catalyst and (ii) an acidic phosphorus-containing additive, with the catalyst (i) being added after, the additive (ii), because of the order of additive employed in the present invention, the reaction rate of the polymerization step (b) is relatively insensitive to the level of additive (ii).

20

In another aspect, the present invention relates to a polyester, and in particular, a poly(ethylene terephthalate) (PET) resin or a modified PET resin which is preferably made by the inventive process. In this regard, the polyester contains elemental phosphorus in an amount not greater than 45 ppm and organic toners in an amount of about 0.5 to about 10 ppm. Moreover, polymer resulting from step (b) is preferably at least substantially free of antimony phosphate compounds. The polyester resin preferably has an intrinsic viscosity of about 0.4 to 1.2 dL/g measured at 25 C by dissolving 250 mg of polyester in 50 mL of a solvent consisting of a 60:40 ratio by weight of phenol and 1,1,2,2-tetrachloroethane.

30

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates the effect on phosphorus level on DEG level of the esterification product when phosphoric acid is added before esterification stage;

5

Fig. 2 illustrates the effect on reaction rate, as represented by time in the polycondensation stage, of changing phosphorus and antimony levels when acidic phosphorus-containing compounds are introduced prior to the antimony catalyst;

10

Fig. 3 illustrates the effect on reaction rate, as represented by time in the polycondensation stage, of changing phosphorus and antimony levels when acidic phosphorus-containing compounds are introduced after the antimony catalyst.

## 15 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to a process for making polyester resins and in particular, poly(ethylene terephthalate), which employs the use of acidic phosphorus-containing additives. The amount, and point of introduction, for the acidic phosphorus-containing additives can be optimized so as to provide for an improved process, e.g., a decreased reaction time, and a desired product, e.g., a polyester having improved clarity.

In one preferred aspect, it has been surprisingly discovered that acidic phosphorus-containing additives such as phosphoric acid, do not react in the same manner as non-acidic phosphorus-containing compounds, such as phosphate triesters. In fact, they can have very different, effects on the polymerization stage. For example, it has been discovered that where acidic phosphorus-containing compounds are introduced prior to certain polymerization catalysts, one can provide for relatively high reaction rates at certain phosphorus levels.

30

It was also surprisingly found that the process of the present invention can provide for the reduction, and possibly even elimination, of antimony phosphate crystals in the resulting polyester. This ability to reduce the amount, size or both of antimony phosphate crystals can effectively reduce the particulate haze in the polyester.

With the foregoing in mind, the polyesters may be prepared in accordance with techniques that are recognized in the art. To this end, polyesters are any crystallizable polyester homopolymer or copolymer, preferably those polyesters suitable for use in packaging, and particularly food packaging.

Suitable polyesters are generally known in the art and may be formed from aromatic dicarboxylic acids, esters of dicarboxylic acids, anhydrides of dicarboxylic esters, glycols, and mixtures thereof. More preferably the polyesters are formed from diacids such as terephthalic acid, isophthalic acid, and 2,6-naphthalenedicarboxylic acid, and mixtures thereof, and diols such as ethylene glycol, diethylene glycol, 1,4-cyclohexane dimethanol, 1,4-butanediol, and mixtures thereof.

As discussed above the process of the present invention can produce the polyesters and "modified" polyesters. By "modified" it is meant that the preferred diacids and/or diols are substituted with one or more diacid or diol components. For example, the preferred diol, e.g., ethylene glycol in the case of PET, is substituted with one or more diols and/or the preferred acid component, e.g., terephthalic acid, in the case of PET, is substituted with one or more acid components.

Specifically, the dicarboxylic acid component of the polyester may optionally be substituted with up to about 20 mole percent of one or more different dicarboxylic acids. Such additional dicarboxylic acids include aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms. Examples of dicarboxylic acids to be included with terephthalic acid

are: phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedi-carboxylic acid, stilbene dicarboxylic acid, cyclohexanedi-acetic acid, 1,12-dodecanedioic acid, diphenyl-4, 4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, mixtures thereof and the like.

In addition, the glycol component may optionally be substituted with up to about 20 mole percent, of one or more different diols other than ethylene glycol. Such additional diols include cycloaliphatic diols preferably having 6 to 20 carbon atoms or aliphatic diols preferably having 3 to 20 carbon atoms. Examples of such diols include: diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, 2,2-bis-(4-hydroxypropoxyphenyl)-propane, 1,2-cyclohexane diol, 1,4-cyclohexanediol, mixtures thereof and the like. Polyesters may be prepared from two or more of the above diols. Moreover, the foregoing diols may be in their cis- form, trans- form or mixtures thereof.

The process of the present invention can employ art-recognized steps or stages in forming polyesters. In the context of the present invention, the preferred stages are:

- (1) an esterification stage, including but not necessarily limited to direct esterification; and
- (2) a polymerization stage, including but not limited to a polycondensation reaction.

Moreover, a prepolymer stage also including but not limited to polycondensation, is preferably performed between the esterification and polymerization stages.

Although the singular may be used in connection with the various stages, each of stages may include one or more steps or substages. For example, the esterification and/or prepolymer stages may each include one or more reaction steps or substages having differing reaction conditions, e.g., progressively lower pressures and  
5 temperature. Finally, although these stages are generally recognized in the art, preferred conditions are set out below for convenience and clarity.

In this regard, the esterification stage typically involves heating a mixture of one or more dicarboxylic acids, preferably aromatic dicarboxylic acids, and one or  
10 more diols under suitable conditions and in the optional presence of esterification catalysts. Examples of such conditions include temperatures in the range of about 200°C to about 300°C, preferably 240°C to about 280°C, and pressures of about 0 to about 100, preferably about 0 to about 50 psig. The optional esterification catalysts  
15 can be used alone or in combination. When used the total amount of catalyst is less than about 200 ppm, more preferably less than 100 ppm, on an elemental basis in the resulting polymer. It is more preferred that no catalyst be employed. Suitable colorants may also be added at this point to control the final color of the polyester. The reaction is typically conducted for about 1 to about 4 hours. It should be understood that generally the lower the reaction temperature, the longer the reaction  
20 will have to be conducted.

The esterification stage typically produces a monomer and oligomer mixture continuously in a series of one or more reactors. Alternately, the monomer and oligomer mixture could be produced in one or more batch reactors.

25

In a prepolymer stage, the mixture of polyester monomer and oligomers undergoes a suitable polymerization step, typically melt-phase polycondensation, to produce a low molecular weight precursor polymer. The precursor polymer is produced in a series of one or more reactors operating at elevated temperatures. This  
30 can involve the a single stage, or one or more substages. To this end, the prepolymer stage can involve the use of one or more reactors operated continuously, one or more

batch reactors or even one or more reaction steps or substages performed in a single reactor vessel.

The precise reaction conditions are dependent upon the nature of the reactants and the final product. However, to facilitate removal of excess glycols, water, alcohols, aldehydes, and other reaction products, the reactors are typically run under a vacuum or purged with an inert gas. Inert gas is any gas which does not cause unwanted reaction or product characteristics at reaction conditions. Suitable gases include, but are not limited to CO<sub>2</sub>, argon, helium and nitrogen. The prepolymer stage is typically conducted at a temperature less than about 300°C, and preferably between about 240°C and about 290°C at a pressure sufficient to aid in removing reaction products such as ethylene glycol.

The next stage, which is the polymerization stage, also typically involves the melt-phase polycondensation of the prepolymer product. Although the polymerization stage typically involves the same basic chemistry as the prepolymer stage, the fact that the size of the molecules, and thus the viscosity differs, means that the reaction conditions also differ. A wide variety of reaction conditions, are employed in the art, and as such they all will not be described here. However, the present invention contemplates the use of the wide range of polymerization options that are recognized in the art as being suitable for use with polyesters.

The primary requirement for the polymerization stage according to the present invention is that it be performed in the presence of both a suitable catalyst and a phosphorus additive. In the context of this invention, the additive is introduced prior to the catalyst. While the exact point of introduction for the additive is not critical as long as the additive can suitably react with the diol(s) prior to introduction of the catalyst. According to the present invention, catalyst is added any point after the additive

In some embodiments, it is preferred that the additive be introduced, during, the esterification stage, or prior to or during a prepolymer stage. It is also preferred that the catalyst be introduced at any point after the additive and preferably, immediately prior to, or during, the prepolymer stage as long as it is introduced before  
5 the polymerization stage and sufficiently after the additive to allow the additive to react with the diol(s). Where more than one reaction step or sub-stage is employed in the prepolymer stage, it is more preferred to have the phosphorus introduced in a substage prior to the substage when the catalyst is added.

10 Where the additive is introduced prior to or during the esterification stage, the amount of DEG can be controlled. That is, the later the additive is introduced the less DEG would be expected to be produced. Steps could be taken to reduce the level of DEG formed. The addition point of the acidic phosphorus-containing additive may be optimized to reduce DEG formation. The rate of diethylene glycol formation is  
15 mainly proportional to the concentration of ethylene glycol (EG) end groups. As esterification progresses, the DEG will increase, and there will be fewer EG end groups. Adding the acidic phosphorus-containing compound later in the process may minimize DEG formation. Moreover, there are a variety of art-recognized techniques for reducing the DEG concentration including that discussed in U.S. Patent No.  
20 5,252,513, which is incorporated by reference in its entirety.

In addition, where the phosphorus additive is added during esterification, it is preferred that the additive be introduced late in the stage, preferably after 90%, more preferably after 95% and still more preferably after 98% conversion in the selected  
25 stage.

As examples of suitable addition sequences where more than one esterification sub-stage is employed, phosphoric acid may be added between the first and second esterification stage while the antimony is added after the second esterification stage  
30 and before the first prepolymer stage. Further, phosphoric acid may be added after the



last esterification stage and before the first prepolymer stage while the antimony is added during the prepolymer stage.

Where more than one reaction step or sub-stage is employed in the prepolymer stage, it is more preferred to have the catalyst introduced prior to the final reaction step a sub-stage in order to provide optimal mixing time prior to the polymerization step.

The preferred polymerization catalyst for use in the process of the present invention is an antimony-based polymerization catalyst. Suitable antimony based catalyst include antimony (III) and antimony (V) compounds recognized in the art and in particular, diol-soluble antimony (III) and antimony (V) compounds. Other suitable compounds include those antimony compounds that react with, but are not necessarily soluble in, the diols, with examples of such compounds including antimony (III) oxide.

Specific examples of suitable antimony catalysts include antimony (III) oxide and antimony (III) acetate, antimony (III) glycolates, antimony (III) ethyleneglycoxide and mixtures thereof, with antimony (III) oxide being preferred.

The preferred amount of catalyst added is that effective to provide an elemental antimony level of between about 75 and about 400 ppm by weight of the resulting polyester.

The phosphorus-containing additive employed in the present invention can be any acidic phosphorus-containing compound recognized in the art. Suitable examples of such additives include phosphoric acid, phosphorous acid, polyphosphoric acid, acidic phosphite esters, acidic phosphate esters such as phosphate mono- and di-esters, and mixtures thereof, among others.

The acidic phosphorus-containing additive is present in an amount effective to provide a desired reaction rate. When a desired amount of acidic phosphorus-containing additive is added prior to the antimony catalyst, the polymerization rate can be largely insensitive to phosphorus level and can even be optimized for certain phosphorus levels. For example, it was found for antimony catalyst corresponding to  
5 elemental antimony levels on the order of 210 ppm, and the phosphorus levels were about 20-25 ppm, reaction rates were comparable or better than reaction rates after the reverse addition order.

10 The acidic phosphorus-containing additive can also be present in an amount effective to provide a polyester resin that is at least substantially free of inorganic compounds that are reaction products of the catalyst and the additive and can cause haze in the polyester. That is, under certain conditions, a polycondensation catalyst(s) and an acidic phosphorus-containing additive(s) can react with each other to produce  
15 certain inorganic compounds, such as antimony phosphate. Such inorganic compounds can cause particulate haze in polyesters.

When acidic phosphorus-containing compounds are added prior to the catalyst in the manner of the present invention, the formation of such inorganic compounds  
20 can also be reduced or even eliminated. When a polycondensation process minimizes the formation of such inorganic compounds, the process is more likely to produce polyesters without undesirable levels of particulate haze, which precludes clarity. Accordingly, the process of the present invention is capable of producing a polyester resin "at least substantially free" of such inorganic compounds, and in particular, at  
25 least substantially free of antimony phosphates.

By "at least substantially free," it is meant that the polyester resin does not include levels of the above-discussed inorganic compounds such as antimony phosphates; that create a particulate haze which can have a negative visual impact  
30 upon the resin melt or articles formed from the resin.

The preferred amount of acidic phosphorus-containing additive is that effective to provide a relatively low elemental phosphorus level, i.e., not greater than about 75 ppm based on the weight of the polyester. Suitable levels fall both in the "high" end of that range, e.g., about 45 to about 75 ppm, "mid" levels of 20-45 ppm, and "low" end, of the range, e.g., less than about 15 ppm. Although the chemistry does not impose a lower limit, the amount is typically not less than 1 ppm. The foregoing amounts are by weight of elemental phosphorus in the resulting polyester.

The phosphorus-containing additive is preferably introduced in a solution of the diol(s). To this end, any concentration that is capably providing the desired phosphorus level can be employed. Suitable concentrations include those greater than about 1 % wt., preferably about 3 to about 15 % by weight of the additive in the diol.

Temperatures for the polymerization stage are generally between about 240°C to about 300°C and a pressure between about 0 and about 2 mm Hg. Once the desired inherent viscosity (I.V.) is reached, the polymer is pelletized. Precursor I.V. is generally below about 0.7 to maintain good color. The target I.V. is generally selected to balance good color and minimize the amount of solid stating which is required. Preferably, the I.V. of a polyester of this invention is from about 0.40 dl/g to about 1.2 dl/g. Inherent viscosity was measured at 25°C using 0.50 grams of polymer per 100 ml of a solvent consisting of 60% by weight phenol and 40% by weight tetrachloroethane.

The resulting polymer can then be subjected to further polymerization reaction, e.g., solid phase polymerization (also know as "solid-stating") by techniques which are known in the art and as such are not described in detail here.

Also, although not required, additives normally used in polyesters may be used if desired. Such additives include, but are not limited to colorants, pigments, carbon black, glass fibers, fillers, impact modifiers, antioxidants, stabilizers, flame retardants, rehear aids, acetaldehyde reducing compounds and the like.

In addition, certain organic toners, e.g., blue and red organic toners, such as those described in U.S. Patents 5,372,864 and 5,384,377, which are incorporated by reference, can be used. As discussed in these U.S. Patents, specific examples of  
5 suitable blue toners include substituted 1,4-bis(2,6-dialkylanilino) anthraquinones) while suitable red toners include anthraquinone and anthrapyridone (3-H-dibenz[f,i]isoquinoline-2,7-dione) compounds. The total amount of organic toners in the polymer is preferably 0.5 to about 10 ppm. To this end, about 0.5 to about 3 ppm of organic red toner(s) and about 1 to about 7 ppm of organic blue toner(s) are more  
10 preferred.

The polyester is preferably devoid of any added cobalt compounds. That is, while certain very minor amounts of certain cobalt compounds may be present in the diacid(s) and/or diol(s) starting materials, no cobalt-containing compounds are added  
15 during the process. Moreover, the polyester is preferably devoid of zinc, gallium, and silicon compounds.

While the resin may also contain small amounts of polyfunctional (comonomers, e.g., trifunctional or tetrafunctional comonomers such as trimellitic  
20 anhydride, trimethylolpropane, pyromellitic dianhydride, pentaerythritol, and other polyester forming polyacids or polyols generally known in the art. The use of such polyfunctional comonomers is optional. That is, they may or may not be present.

The polyesters according to the present invention can be used in forming a  
25 variety of articles including sheets, films, tubing, profiles, preforms, fibers, woven and shaped articles, such as containers, and thermoformed articles such as trays and the like.

The present invention will now be described in terms of the following example  
30 which example are offered to illustrate the invention. The examples, however, in no way limit the scope of the invention.

## EXAMPLES

### A. Esterification Procedure

5           Terephthalic acid (TPA) was esterified with plant grade ethylene glycol (EG) and distilled cyclohexanedimethanol (CHDM), where the CHDM content of the copolyester was one and a half mole percent of the total glycols. The esterification was done in a continuous unit and was followed by batch-wise polycondensation. The  
10 esterification was carried out in two continuous reactors connected in series (R1 and R2). A third vessel (R3) was used as a flash tank and for collection of the esterification product. The fixed volume reactors had approximately a 2:1 volume ratio with 2230 mL in R1 and 1100 mL in R2. The feed mole ratio of total glycols to terephthalic acid was 1.35. The amount of CHDM in the feed was 1.5 mole percent of  
15 the terephthalic acid in the feed slurry, with the excess diol in the feed slurry being ethylene glycol. Slurry ingredients were mixed in a blender and added to a feed tank. The feed rate was 10 mL/min. The temperature target in R1 was 262 deg. C. The temperature target in R2 was 267 deg. C. The pressure targets for R1 and R2 were 36.5 PSIG and 18.5 PSIG, respectively. Substantially all the ethylene glycol vaporized  
20 from R1 was condensed and returned directly to R1.

          In the esterification phase of the designed experiment, the factors being varied were additive type and level. The additive was mixed into the TPA/glycol slurry. For a summary of the additive or catalyst type and level target for each run, see the table  
25 below.

Sample	Additive/catalyst	Level Target (ppm)	Phosphorus Source
1	None		
2	P	30	H <sub>3</sub> PO <sub>4</sub>
3	P	50	H <sub>3</sub> PO <sub>4</sub>
4	P	30	H <sub>3</sub> PO <sub>4</sub>
5	P	10	H <sub>3</sub> PO <sub>4</sub>
6	P	62	H <sub>3</sub> PO <sub>4</sub>
7	P	30	H <sub>3</sub> PO <sub>4</sub>
8	Sb	200	
9	Sb	250	
10	Sb	200	
11	Sb	150	
12	Sb	250	
18	Sb	150	
19	P	30	H <sub>3</sub> PO <sub>4</sub>
20	P	10	H <sub>3</sub> PO <sub>4</sub>

The additive or catalyst solutions were made per the following procedures. A phosphorus concentration target of 3.5 wt. % was used for the phosphorus solution.

- 5 Phosphoric acid (13.03 g of 85 %, Food Grade, FMC) was weighed into a tared glass bottle. Ethylene glycol was added until the total solution weight was 100.00 g. A magnetic stir bar was added, and the mixture was stirred.

- 10 A solution of antimony oxide in ethylene glycol was made with a target antimony concentration of 1.2 wt. %. Antimony oxide (7.37 g, Fisher) was added into a tared, three-necked, 1-L round-bottomed flask. Ethylene glycol was added until the total solution weight was 500.00 g. The flask was fitted with a heating mantle, condenser, a stopper and a paddle stirrer. The condenser was connected to a nitrogen source and vented through a bubbler to keep air from entering the system. An
- 15 insulating jacket was placed on the exposed upper portion of the flask. The flask was

heated with stirring until the EG was refluxing vigorously. The mixture was held at reflux for at least 3 hours. The mixture was cooled and filtered through a 0.22 micron cellulose acetate, supported plain filter by Micron Separations, Inc.

5 Oligomers made with a given additive or catalyst were produced in the continuous unit in a block to minimize the magnitude of the transition required. Within a block for a given additive or catalyst, the target levels were randomized. In the interest of minimizing transitions, the highest target level was not run at the beginning of a block. The unit was run for twenty-four hours to make each oligomer.  
10 Product was collected in a nitrogen-purged, covered, steel beaker, surrounded by dry ice. The beaker was changed about every three hours. The materials from the last three beakers – representing the last 9 hours of a run – were ground and analyzed. Before polymerization, the beakers judged to be comparable were combined in a large bag with shaking.

15

The carboxyl end groups were determined by titration with base. Additive and catalyst levels were measured by X-ray fluorescence (XRF). Degree of polymerization and mole % reacted CHDM were obtained by NMR spectroscopy of a phenol and 1,1,2,2-tetrachloroethane solution. Percent conversion calculations combined carboxyl  
20 end groups and NMR data. After samples were hydrolyzed and silylated, the weight percent of diethylene glycol was measured via a gas chromatography method. Molecular weights were determined by gel permeation chromatography.

#### Example 1: Esterification in the Presence of a Target of 150 ppm Antimony

25 The slurry put in the feed tank consisted of 3270 g of Amoco TPA, 1585 g of EG, 42.6 g of CHDM, and 46.3 g of antimony solution (x-ray fluorescence measurement: 0.0124 g antimony/g solution). Analyses on the esterification product (Sample 18) resulted in the following data: carboxyl end groups of 370 meq KOH/kg, a percent conversion of carboxyl end groups to ester end groups of 96.3%, a degree of  
30 polymerization of 5.6, an antimony level of 135 ppm, a diethylene glycol (DEG) level

of 1.46 wt. %, a reacted CHDM level of 1.43 mole %, a number-averaged molecular weight of 913 g/mole, and a weight-averaged molecular weight of 1621 g/mole.

Example 2: Esterification in the Presence of a Target of 250 ppm Antimony

5        The slurry put in the feed tank consisted of 3270 g of Amoco TPA, 1556 g of EG, 42.6 g of CHDM, and 76.5 g of antimony solution (x-ray fluorescence measurement: 0.0125 g antimony/g solution). Analyses on the esterification product (Sample 9) resulted in the following data: carboxyl end groups of 378 meq KOH/kg, a percent conversion of carboxyl end groups to ester end groups of 96.2%, a degree of  
10    polymerization of 5.5, an antimony level of 232 ppm, a diethylene glycol (DEG) level of 1.48 wt. %, a reacted CHDM level of 1.43 mole %, a number-averaged molecular weight of 875 g/mole, and a weight-averaged molecular weight of 1640 g/mole.

Example 3: Esterification in the Presence of a Target of 10 ppm Phosphorus

15        The slurry put in the feed tank consisted of 3270 g of Amoco TPA, 1630 g of EG, 42.6 g of CHDM, and 1.06 g of phosphoric acid solution (x-ray fluorescence measurement: 0.0360 g phosphorus/g solution). Analyses on the esterification product (Sample 20) resulted in the following data: carboxyl end groups of 343 meq KOH/kg, a percent conversion of carboxyl end groups to ester end groups of 96.5%, a degree of  
20    polymerization of 5.3, a phosphorus level of 7 ppm, a diethylene glycol (DEG) level of 1.64 wt. %, a reacted CHDM level of 1.33 mole %, a number-averaged molecular weight of 900 g/mole, and a weight-averaged molecular weight of 1606 g/mole.

Example 4: Esterification in the Presence of a Target of 62 ppm Phosphorus

25        The slurry put in the feed tank consisted of 3270 g of Amoco TPA, 1625 g of EG, 42.6 g of CHDM, and 6.57 g of phosphoric acid solution (x-ray fluorescence measurement: 0.0361 g phosphorus/g solution). Analyses on the esterification product (Sample 6) resulted in the following data: carboxyl end groups of 365 meq KOH/kg, a percent conversion of carboxyl end groups to ester end groups of 96.3%, a degree of  
30    polymerization of 5.7, a phosphorus level of 48 ppm, a diethylene glycol (DEG) level



of 1.95 wt. %, a reacted CHDM level of 1.30 mole %, a number-averaged molecular weight of 899 g/mole, and a weight-averaged molecular weight of 1660 g/mole.

Per examples 3 and 4, as the phosphoric acid level increased, there was an  
5 increase in the DEG level of the esterification product. This trend is illustrated in  
*Figure 1*, which depicts DEG level versus phosphorus level.

### B. Polymerization Procedure

10 The melt-phase polymerization stage of the designed experiment was run in  
random order. Esterification products were prepared per the preceding section.  
Ground esterification product (206 g) was weighed into a one-liter, single-necked,  
round-bottomed flask. A 316L stainless steel paddle stirrer and a glass polymer head  
were attached to the flask. After attaching the polymer head to a side arm and a purge  
15 hose, two nitrogen purges were completed.

The polymerization reactor was operated under the control of a CAMILE™  
automation system. After a molten bath of Belmont metal was raised to surround the  
flask, the CAMILE™ array was initiated. See the following table for the  
polymerization conditions.

20 In a CAMILE™ array, a ramp is defined as a linear change of vacuum,  
temperature or stir speed during the specified stage time. After the melting stage (# 2)  
ended, a 5-minute catalyst addition stage (# 3) began, and the appropriate additive or  
catalyst solution was added within the last minute of this stage. The additive and  
catalyst solutions were prepared as described in the Esterification Procedure section.  
25 The stirring system was automatically calibrated after stage four and prior to stage  
five. The finisher stage (#13) was terminated when the power reached 4.75% three  
times. Polymers were cooled to ambient temperature.

CAMILE Polymerization Array

Stage Number	Stage Time (min.)	Temp. (°C)	Vacuum (torr)	Stir Speed (rpm)
1	0.0	265	760	0
2	15	265	760	150 *
3	5.0	265	760	200 *
4	10	265	15 *	200
5	1.0	265	15	100 *
6	47	275 *	15	100
7	1.0	275	15	50*
8	40	275	15	50
9	5.0	275	1.5 *	50
10	5.0	275	0.5 *	50
11	5.0	275	0.5	50
12	1.0	275	1.5 *	50
13	Variable	275	1.5	50

\* = Ramp

- 5        The polymers were chopped and ground to pass a 3 mm screen. Ground polymers were shaken on a 40-mesh sieve fitted with a lid and pan. The lid and the pan were removed. A second 40-mesh sieve was placed on top of the first. Compressed air was blown through the pair of sieves. This dust removal process reduced the number of fines that adhered to larger particles during the sieving process.
- 10      The fines would solid-phase polymerize quickly and adversely affect comparisons. The +40 mesh portion of each polymer was shaken through a series of sieves: 10, 12, 14, 16, 18 and 20 mesh. The polymer fraction on each sieve was weighed. To conserve the +12 to +20 mesh portion of each polymer to be used in solid stating, - 20/+40 mesh portion of each polymer was used for precursor testing, except for color.

For each sieved polymer, the weights on each sieve (except the 10 mesh) were compared. For each sieve size, the smallest weight among the samples was noted. Combining the smallest weight available for each sieve size, a weight distribution common to all the samples was defined. By minimizing particle size differences among the preparative samples, the standard blend enabled more internally consistent solid-state studies. This standard blend had a total weight of 80.5 g where 8.4 grams were -10/+12 mesh, 32.54 grams were -12/+14 mesh, 20.27 grams were -14/+16 mesh, 14.48 grams were -16/+18 mesh, and 4.81 grams were -18/+20 mesh grinds. Color was measured on the precursor blend.

10

The inherent viscosity (IV) was measured at 25 deg. C by dissolving 0.50 grams of polymer in 100 mL of 60% phenol and 40% 1,1,2,2-tetrachloroethane by weight. Additive and catalyst levels were measured by X-ray fluorescence (XRF). The carboxyl end groups were determined by titration with base. Color was measured using a HunterLab Color test, which was reported in CIELAB units. The diethylene glycol (DEG) level was measured by dissolving 22 to 28 mg of polymer in a solvent mixture consisting of 70% chloroform-d and 30% trifluoroacetic acid-d and obtaining the NMR spectrum on a 500 MHz instrument.

20

Example 5: Polymerization of Esterification Product #18 (135 ppm Sb) with Prepolymer Addition of 7 ppm of Phosphorus

Ground esterification product (Sample 18, 206 g) was weighed into a one-liter, single-necked, round-bottom flask. Phosphoric acid (0.03 mL of 3.60 wt./wt. % P solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 93 minutes. Analyses on the polymer resulted in the following data: IV of 0.552 dL/g, an antimony level of 117 ppm, a phosphorus level of 8 ppm, carboxyl end groups of 14.0 meq/kg, a L\* color of 89.3, an a\* color of -1.1, a b\* color of 4.5, and a DEG level of 1.70 wt.%.

30

Example 6: Polymerization of Esterification Product #18 (135 ppm Sb) with  
Prepolymer Addition of 49 ppm of Phosphorus

Ground esterification product (Sample 18, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Phosphoric acid (0.27 mL of 3.60 wt./wt. % P solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 224 minutes (3-7 hrs). Analyses on the polymer resulted in the following data: IV of 0.564 dL/g, an antimony level of 140 ppm, a phosphorus level of 48 ppm, carboxyl end groups of 14.1 meq/kg, a L\* color of 89.7, an a\* color of -1.0, a b\* color of 5.2, and a DEG level of 1.73 wt.%.

Example 7: Polymerization of Esterification Product #9 (232 ppm Sb) with  
Prepolymer Addition of 7 ppm of Phosphorus

Ground esterification product (Sample 9, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Phosphoric acid (0.03 mL of 3.60 wt./wt. % P solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 60 minutes. Analyses on the polymer resulted in the following data: IV of 0.551 dL/g, an antimony level of 211 ppm, a phosphorus level of 7 ppm, carboxyl end groups of 11.0 meq/kg, a L\* color of 89.3, an a\* color of -1.3, a b\* color of 4.7, and a DEG level of 1.70 wt.%.

Example 8: Polymerization of Esterification Product #9 (232 ppm Sb) with  
Prepolymer Addition of 49 ppm of Phosphorus

Ground esterification product (Sample 9, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Phosphoric acid (0.27 mL of 3.60 wt./wt. % P solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 124 minutes. Analyses on the polymer resulted in the following data: IV of 0.566 dL/g, an antimony level of 233 ppm, a phosphorus level of 50 ppm, carboxyl end groups of 12.9 meq/kg, a L\* color of 89.7, an a\* color of -1.0, a b\* color of 4.1, and a DEG level of 1.70 wt.%.

Example 9: Polymerization of Esterification Product #20 (7 ppm P) with Prepolymer  
Addition of 135 ppm of Antimony

Ground esterification product (Sample 20, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Antimony glycolate (2.3 mL of 1.11 wt./wt. % Sb solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 104 minutes. Analyses on the polymer resulted in the following data: IV of 0.557 dL/g, an antimony level of 122 ppm, a phosphorus level of 8 ppm, carboxyl end groups of 10.9 meq/kg, a L\* color of 89.8, an a\* color of -1.3, a b\* color of 5.5, and a DEG level of 1.82 wt.%.

Example 10: Polymerization of Esterification Product #6 (48 ppm P) with Prepolymer  
Addition of 135 ppm of Antimony

Ground esterification product (Sample 6, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Antimony glycolate (2.3 mL of 1.11 wt./wt. % Sb solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 119 minutes. Analyses on the polymer resulted in the following data: IV of 0.567 dL/g, an antimony level of 123 ppm, a phosphorus level of 43 ppm, carboxyl end groups of 14.2 meq/kg, a L\* color of 89.3, an a\* color of -0.9, a b\* color of 5.1, and a DEG level of 2.23 wt.%.

Example 11: Polymerization of Esterification Product #20 (7 ppm P) with Prepolymer  
Addition of 232 ppm of Antimony

Ground esterification product (Sample 20, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Antimony glycolate (4.3 mL of 1.11 wt./wt. % Sb solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 76 minutes. Analyses on the polymer resulted in the following data: IV of 0.567 dL/g, an antimony level of 231 ppm, a phosphorus level of 9 ppm, carboxyl end groups of 9.9 meq/kg, a L\* color of 89.4, and a \* color of -1.3, a b\* color of 5.2, and a DEG level of 1.80 wt.%.

Example 12: Polymerization of Esterification Product #6 (48 ppm P) with Prepolymer Addition of 232 ppm of Antimony

Ground esterification product (Sample 6, 206 g) was weighed into a one-liter, single-necked round-bottom flask. Antimony glycolate (4.0 mL of 1.19 wt./wt. % Sb solution) was added within the last minute of stage 3. The finisher time (length of stage 13) was 88 minutes. Analyses on the polymer resulted in the following data: IV of 0.543 dL/g, an antimony level of 214 ppm, a phosphorus level of 39 ppm, carboxyl end groups of 10.5 meq/kg, a L\* color of 87.9, an a\* color of -0.7, a b\* color of 5.3, and a DEG level of 2.20 wt. %.

Per examples 5-8, when phosphoric acid was added to esterification product containing antimony (antimony early & phosphoric acid late), the finisher time increased significantly with increasing phosphorus level, especially at the lower antimony level. In contrast, examples 9-12 illustrated that when antimony was added to esterification product containing phosphorus from phosphoric acid i.e., (phosphoric acid early & antimony late), the finisher time was relatively insensitive to phosphorus level. As the additive level increases, the melt-phase production rate of this process will be faster than that of a process adding antimony early and phosphoric acid late. The observed finisher times, the phosphorus addition points, and the measured values of both antimony and phosphorus were used to generate a response surface model with JMP TM statistical software. From the response surface model, the contour plots shown in *Figures 2 & 3* were generated. The numbers on these figures correspond to finisher time in minutes. *Figure 2* illustrates the effect on finisher time of changing phosphorus levels and antimony levels when phosphoric acid is added just prior to the prepolymer stage. *Figure 3* illustrates the effect on finisher time of changing phosphorus levels and antimony levels when phosphoric acid is added up front to the TPA/EG/CHDM paste prior to the esterification stage.

Per examples 9-12, when phosphoric acid was added before the esterification stage, the diethylene glycol level in the polyester was sensitive to the level of additive

present. Therefore, the maximum level of phosphoric acid used can be determined by the maximum level of diethylene glycol (DEG) that could be tolerated.

### C. Solid-phase Polymerization

5

Two metal solid-staters were used to solid-phase polymerize the precursors. A CAMILE™ system controlled conditions in the solid-staters – except for nitrogen flow rate, which was controlled manually with a rotameter. Heated nitrogen passed through a frit that supported a bed of precursor. The set point for the nitrogen  
10 temperature just below the frit was 205 °C, and the nitrogen flow rate was 14 standard cubic feet per hour. Solid-stating rate studies were done in a random order different than that used for the melt-phase polymerizations. Prior to each solid-stating rate study, the standard particle size blend was thoroughly mixed, and then a 30-gram portion of the blend was removed and poured into a metal solid-stater. The bed was  
15 made level.

A sample of approximately 0.6 grams was removed every 30 minutes for six hours. Before each sample was taken, the bed was stirred for 30 seconds using a wire whisk attached to a rod. The stirring mixed the sample bed horizontally and vertically  
20 to minimize the effect on IV of particle location in the bed. After a sample of about 0.6 grams was removed, the bed was leveled.

After each rate study was complete, about 22 grams of polymer remained in the solid-stater; this material was isolated and analyzed. These samples had inherent  
25 viscosities, which ranged from 0.75 to 0.77 dL/g.

As each rate study was completed, samples were submitted for IV analysis. From the IV data, the solid-phase polymerization time to reach the product IV (0.68 dL/g) for each precursor was determined from a plot of IV as a function of time. For  
30 each precursor, the solid-stating time to 0.68 IV determined the length of the preparative solid-stating runs.

Preparative solid-stating runs were performed at the same nitrogen temperature and flow rate used during the rate studies. A random run order was generated for the preparative solid-phase polymerizations. For each precursor, fifty grams of the standard particle size blend were used for the solid-phase preparative run. Although  
5 no samples were taken, the bed was stirred and leveled every 30 minutes. The preparative samples were submitted for the following tests: IV, color, acetaldehyde generation, and solution haze.

10 The acetaldehyde generation test was performed at 295°C. Ten grams of polymer were dried at 120°C overnight. The polymer was placed in a melt indexer for 5 minutes at 295°C, extruded and quenched. The polymer was cryogenically ground and sieved ( $\leq 20$  mesh particle size). An inert gas was passed across the sample ( $0.50 \pm 0.05$  grams) at 150°C for 10 minutes. The gas was then sent to a trap cooled with  
15 liquid nitrogen. The trap was then heated to 300°C, and the acetaldehyde was swept into a gas chromatograph for measurement.

The solution haze was measured by dissolving the polymer (10.0 g) in a mixture of methylene chloride and hexafluoro isopropyl alcohol (130 mL, 70:30 v/v).  
20 The turbidity of the solution was measured with a Hach Ratio Nephelometric Turbidimeter. The mixtures were centrifuged to isolate the particulates when the solution haze values were  $\geq 5$  ntu, except for Examples 13 and 15. The particulates were analyzed by x-ray diffraction (XRD) to identify crystalline species and by energy dispersive spectroscopy (EDS) to identify the elements, present, including those in  
25 amorphous species.

Example 13: Solid Stating of Polymer with 117 ppm of Antimony and 8 ppm of Phosphorus (Antimony Early/Phosphoric Acid Late)

Polymer was solid stated for 1 hour and 48 minutes. Analyses on the polymer resulted  
30 in the following data: IV of 0.665 dL/g, a L\* color of 88.8, an a\* color of -1.0, a b\* color of 4.6, an acetaldehyde generation at 295°C of 12.5 ppm, and a solution haze



value of 4.5 ntu. Per XRD, the particulates contained antimony oxide. EDS indicated that antimony (silicon, copper, iron) was present in the particulates.

Example 14: Solid Stating of Polymer with 140 ppm of Antimony and 48 ppm of Phosphorus (Antimony Early/Phosphoric Acid Late)

Polymer was solid stated for 3 hour and 10 minutes. Analyses on the polymer resulted in the following data: IV of 0.673 dL/g, a L\* color of 88.9, an a\* color of -1.0, a b\* color of 5.2, an acetaldehyde generation at 295°C of 11.5 ppm, and a solution haze value of 4.4 ntu.

Example 15: Solid Stating of Polymer with 211 ppm of Antimony and 7 ppm of Phosphorus (Antimony Early/Phosphoric Acid Late)

Polymer was solid stated for 1 hour and 51 minutes. Analyses on the polymer resulted in the following data: IV of 0.662 dL/g, an acetaldehyde generation at 295°C of 15.1 ppm, and a solution haze value of 4.7 ntu. Per XRD, the particulates contained antimony oxide. EDS indicated that antimony was present in the particulates.

Example 16: Solid Stating of Polymer with 223 ppm of Antimony and 50 ppm of Phosphorus (Antimony Early/Phosphoric Acid Late)

Polymer was solid stated for 2 hours and 36 minutes. Analyses on the polymer resulted in the following data: IV of 0.686 dL/g, a L\* color of 89.2, an a\* color of -1.0, a b\* color of 3.9, an acetaldehyde generation at 295°C of 12.2 ppm, and a solution haze value of 6.8 ntu. Per XRD, the particulates contained antimony oxide and antimony phosphate. EDS indicated that antimony and phosphates were present in the particulates.

Example 17: Solid Stating of Polymer with 8 ppm of Phosphorus and 122 ppm of Antimony (Antimony Late/Phosphoric Acid Early)

Polymer was solid stated for 2 hours and 7 minutes. Analyses on the polymer resulted in the following data: IV of 0.673 dL/g, a L\* color of 89.0, an a\* color of -1.2, a b\*

color of 5.4, an acetaldehyde generation at 295°C of 11.9 ppm, and a solution haze value of 4 ntu.

Example 18: Solid Stating of Polymer with 9 ppm of Phosphorus and 231 ppm of Antimony (Antimony Late/Phosphoric Acid Early)

Polymer was solid stated for 1 hour and 45 minutes. Analyses on the polymer resulted in the following data: IV of 0.684 dL/g, a L\* color of 88.3, an a\* color of -1.4, a b\* color of 5.4, an acetaldehyde generation at 295°C of 11.7 ppm, and a solution haze value of 5 ntu. Per XRD, the particulates contained antimony oxide. EDS indicated that antimony was present in the particulates.

Example 19: Solid Stating of Polymer with 43 ppm of Phosphorus and 123 ppm of Antimony (Antimony Late/Phosphoric Acid Early)

Polymer was solid stated for 1 hour and 47 minutes. Analyses on the polymer resulted in the following data: IV of 0.673 dL/g, a L\* color of 88.6, an a\* color of -0.9, a b\* color of 5.5, an acetaldehyde generation at 295°C of 14.0 ppm, and a solution haze value of 3.1 ntu.

Example 20: Solid Stating of Polymer with 39 ppm of Antimony and 214 ppm of Phosphorus (Antimony Late/Phosphoric Acid Early)

Polymer was solid stated for 1 hour and 34 minutes. Analyses on the polymer resulted in the following data: IV of 0.678 dL/g, a L\* color of 88.1, an a\* color of -0.83, a b\* color of 5.2, an acetaldehyde generation at 295°C of 14.1 ppm, and a solution haze value of 3.9 ntu.

Per Example 16, when phosphoric acid was added to an esterification product containing antimony, antimony phosphate and antimony oxide were found in the particulates isolated from the solution haze sample. Antimony phosphate can cause haze in polyesters. Per Example 18, when antimony was added to an esterification product containing phosphorus from phosphoric acid, only antimony oxide was found in the particulates isolated from the solution haze sample. Potential haze problems

due to antimony phosphate formation were precluded by adding phosphoric acid early and antimony late.

Example 21: A Phosphate Triester as the Phosphorus Source

5 When a phosphate triester like tri-t-butyl phosphate is the phosphorus source, the trends are different than those observed for phosphoric acid. When the antimony is added early and the phosphate triester is added late, the melt-phase finisher time is relatively insensitive to the phosphorus level. The dramatic increase in finisher time with increasing phosphorus level for early antimony/late phosphoric acid addition is  
10 not seen when the phosphorus source is a phosphate triester. When the antimony is added early and the phosphate triester is added late, antimony oxide alone is found in the particulates isolated from solution haze samples. In contrast to the situation with late addition of phosphoric acid, particulate haze from antimony phosphate is not a concern when a phosphate triester is added late.

15

When the phosphate triester is added early and the antimony is added late, the melt-phase finisher time increases with increasing phosphorus level. The stability in finisher time with increasing phosphorus level for early phosphoric acid/late antimony addition is not seen when the phosphorus source is a phosphate triester.

20

While the invention has been described in terms of various preferred embodiments thereof, it should be understood that various modifications, changes, substitutions, omissions and the like may be made without departing from the spirit of the invention. Thus, the scope of the invention is limited only by the scope of the  
25 following claims including equivalents thereof.

CLAIMS

What is claimed is:

1. A process for making polyester resin comprising
  - (a) esterifying at least one dicarboxylic acid component and at least one diol component; and
  - (b) polymerizing the product of step (a) under conditions effective to provide a polyester resin,wherein:
  - (1) polymerization step (b) occurs in the presence of (i) an antimony-based polymerization catalyst and (ii) an acidic phosphorus-containing additive, with the catalyst (i) being added after the additive (ii), and
  - (2) the acidic phosphorus containing additive (ii) is added sufficiently before the polycondensation catalyst (i) such that the additive (ii) can react with the at least one diol.
2. A process for making polyester resin comprising
  - (a) esterifying at least one dicarboxylic acid component and at least one diol component; and
  - (b) polymerizing the product of step (a) under conditions effective to provide a polyester resin,wherein:
  - (1) polymerization step (b) occurs in the presence of (i) an antimony-based polymerization catalyst and (ii) an acidic phosphorus-containing additive, with the catalyst (i) being added after the additive (ii), and

- (2) the acidic phosphorus containing additive (ii) is selected such that the reaction rate of the polymerization step (b) is relatively insensitive to the level of additive (ii).
3. The process according to claim 2, wherein the length of time between the addition of the additive and the catalyst is sufficient to allow a reaction between the additive and the diol.
4. The process according to claim 1, wherein the additive (ii) is added prior to a point in the step (a) where the at least one diol will have a partial pressure such that the at least one diol will boil away.
5. The process according to claim 4 wherein the partial pressure of the diol compound is not less than about 300 Torr.
6. The process according to claim 1, further comprising:
  - (a) solid-phase polymerization of the polyester resin from step (b).
7. The process according to claim 1, further comprising a prepolymer reaction stage between the esterification step (a) and polymerization reaction (b).
8. The process according to claim 7, wherein the additive (ii) is added immediately prior to, or during the prepolymer stage.
9. The process according to claim 7 wherein the catalyst (i) is added immediately prior to, during, or after the prepolymer stage, but prior to the polymerization step.
10. The process according to claim 1, wherein the additive (ii) is added immediately prior to, or during the esterification step (a).

11. The process according to claim 5, wherein the polyester resin is a poly(ethylene terephthalate) (PET) resin or a modified PET resin.
12. The process according to claim 1, wherein the at least one dicarboxylic acid comprises terephthalic acid.
13. The process according to claim 12 wherein the terephthalic acid is present in an amount of from about 80 mole % to about 95 mole %.
14. The process according to claim 1, wherein the at least one diol component comprises a glycol having from about 2 to about 10 carbon atoms.
15. The process according to claim 1, wherein the at least one diol component comprises ethylene glycol.
16. The process according to claim 15 wherein the ethylene glycol is present in an amount of from about 80 mole % to about 95 mole %.
17. The process according to claim 1, wherein the polyester resin is modified with at least one additional diacid component is selected from aromatic dicarboxylic acids having 8 to 14 carbon atoms, aliphatic dicarboxylic acids having 4 to 12 carbon atoms, cycloaliphatic dicarboxylic acids having 8 to 12 carbon atoms and mixtures thereof, wherein the additional diacid component(s) are present in the amount of about 1 mole % to 20 mole %.
18. The process according to claim 17, wherein the at least one additional dicarboxylic acid component is phthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, 1,3-cyclohexanedicarboxylic acid, diphenyl-4,4'-dicarboxylic acid, stilbenedicarboxylic acid, succinic acid, glutaric acid, adipic acid, sebacic acid, cyclohexane diacetic acid, azelacic acid or 1,12-dodecanedioic acid.

19. The process according to claim 1 wherein the polyester resin is modified with at least one additional diol component selected from cycloaliphatic diols having 6 to 20 carbon atoms, aliphatic diols having 3 to 20 carbon atoms, and mixtures thereof, wherein the additional diol component(s) are present in the amount of about 1 mole % to 20 mole %.
20. The process according to claim 19, wherein the at least one additional diol component is 1,4-cyclohexanedimethanol (CHDM), diethylene glycol, triethylene glycol, 1,2-propanediol, 1,3-propanediol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentanediol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, 2,2-bis-(4-hydroxypropoxyphenyl)-propane, 1,2-cyclohexanediol, 1,4-cyclohexanediol or mixtures thereof.
21. The process according to claim 1, wherein the polymerization step (b) is a polycondensation reaction and the catalyst (i) is a polycondensation catalyst.
22. The process according to claim 1 wherein the antimony-based catalyst (i) is a diol-soluble compound of antimony (III) or antimony (V) or a compound of antimony (III) or antimony (V) that becomes soluble upon reaction with the diol.
23. The process according to claim 1, wherein the antimony-based catalyst (i) is selected from the group of antimony (III) oxide, antimony (III) acetate, antimony (III) glycolates, antimony (III) ethyleneglycoxide and mixtures thereof.

24. The process according to claim 1, wherein the antimony-based catalyst (i) is antimony oxide that is present in an amount effective to provide elemental antimony of from about 75 ppm to about 400 ppm in the polymer.
25. The process according to claim 1, wherein the acidic phosphorus-containing additive (ii) comprises phosphoric acid, phosphorous acid, polyphosphoric acid, acidic phosphate esters or mixtures thereof.
26. The process according to claim 1, wherein the acidic phosphorus-containing additive (ii) comprises phosphoric acid.
27. The process according to claim 1, wherein the acidic phosphorus-containing additive (ii) is present in the amount between about 20 and about 45 ppm of elemental phosphorus based on the weight of the polymer.
28. The process according to claim 1, wherein the acidic phosphorus-containing additive (ii) is present in the amount of less than about 15 ppm of elemental phosphorus based on the weight of the polymer.
29. The process according to claim 1 wherein catalyst residue from step (b) is at least substantially free of antimony phosphate compounds.
30. The process according to claim 1, wherein the polyester resin has an intrinsic viscosity of about 0.4 to 1.2 dL/g measured at 25 C by dissolving 250 mg of polyester in 50 mL or a solvent consisting of a 60:40 ratio by weight of phenol and tetrachloroethane.
31. The process according to claim 1, wherein the polymerization step (b) is performed in the absence of added cobalt compound(s).



32. The process according to claim 1, wherein the polymerization step (b) is performed in the presence of at least one organic toner selected from among red organic toners, and blue organic toners.
33. A polyester product produced by the process according to claim 1.
34. A polyester containing (a) elemental phosphorus present in an amount not greater than about 75 ppm and (b) at least one organic toner selected from among organic blue toners and organic red toners, which toner(s) are present in an amount of about 0.5 to about 10 ppm.
35. The polyester according to claim 34 wherein the elemental phosphorus is present in an amount less than about 15 ppm based on elemental phosphorus.
36. The polyester according to claim 34 having at least one organic red toner present in an amount of about 0.5 to about 3 ppm.
37. The polyester according to claim 34 having at least one organic blue toner present in an amount of about 1 to about 7 ppm.

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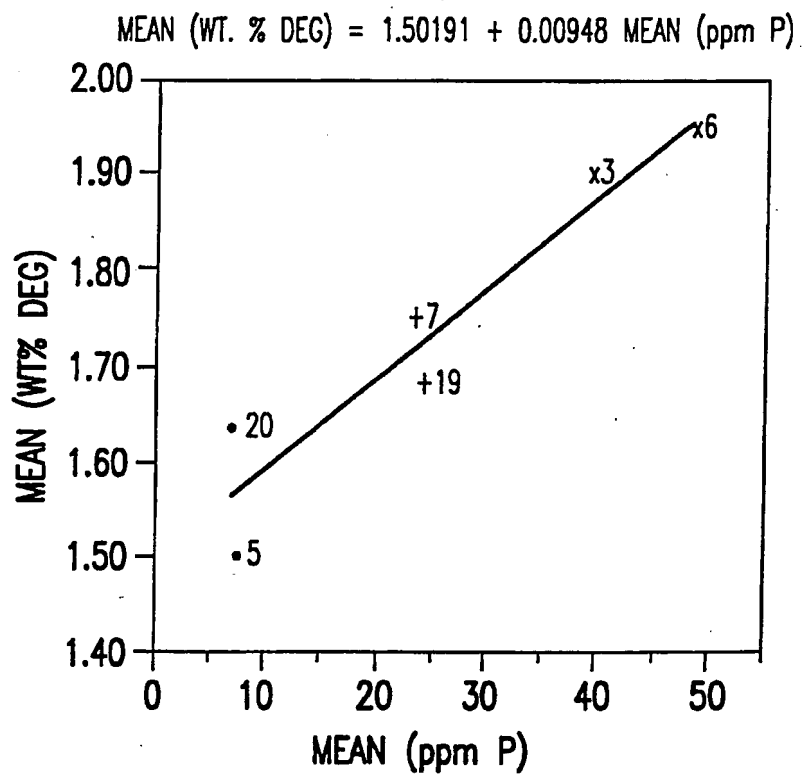


FIG.1

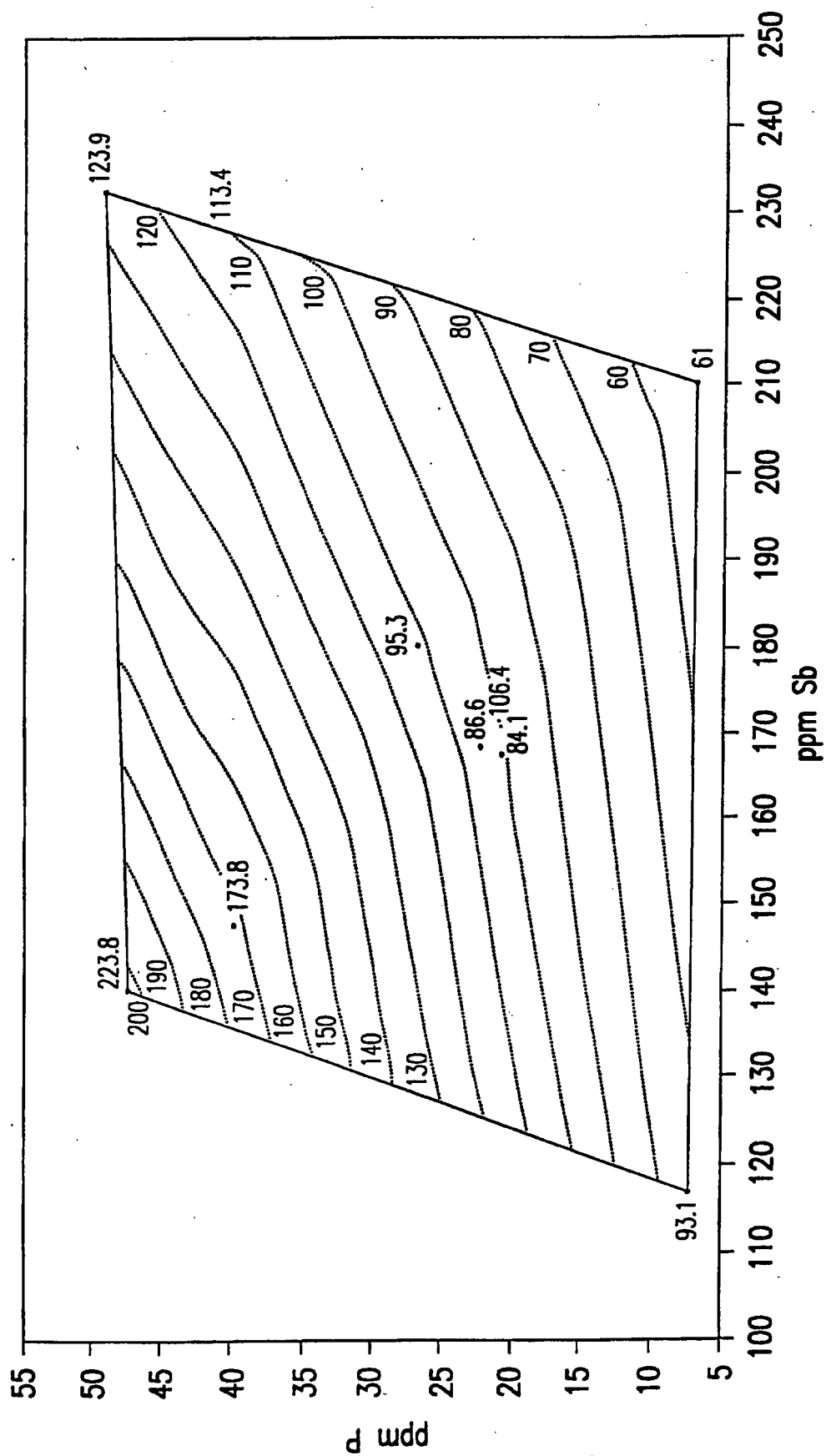


FIG. 2

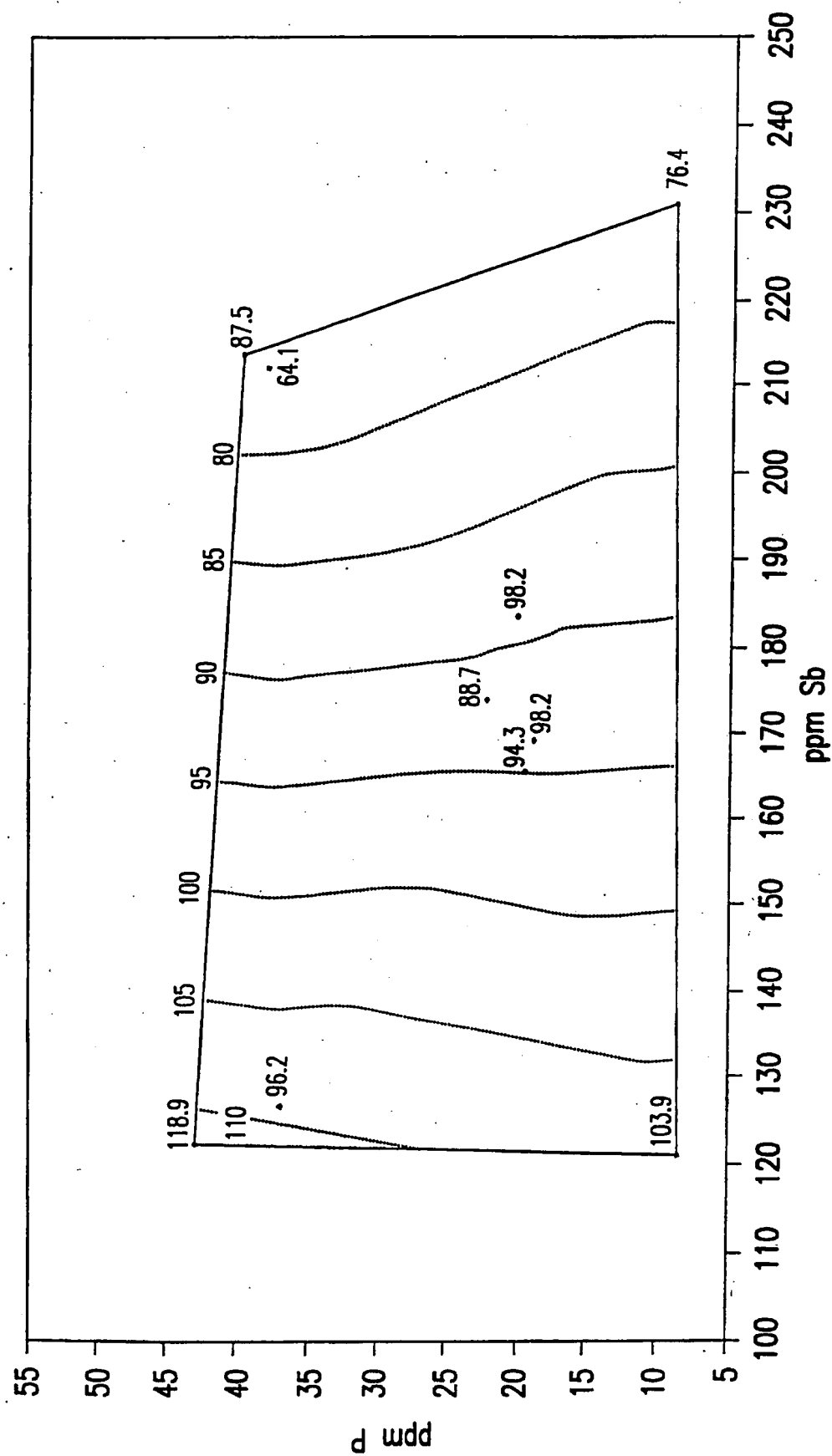


FIG.3

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/19385

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08G63/86 C08G63/82 C08G63/78

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 061 414 A (GOODYEAR TIRE & RUBBER) 29 September 1982 (1982-09-29)	1-7, 9-12, 14, 15, 21-26, 28, 30, 33
Y	claims 6-9; example; table I page 12, line 13 -page 14, line 11 & US 4 499 226 A cited in the application ----- -/--	13, 17-20, 31, 32

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

20 April 2000

Date of mailing of the international search report

04/05/2000

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/19385

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Y	claims 5,6; example 1 & US 5 235 027 A cited in the application	13, 17-20, 31,32
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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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